**Final Report
for the period
October 1983 to
March 1984**

Columbium Chamber
Fabrication Study

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Space Division, Air Force Systems Command
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FOREWORD

This report covers research performed under Air Force contract F04611-83-C-0057, Job Order Number 305800 QC by Aerojet TechSystems Company during the period October 1983 to March 1984. Lt J. Man served as Project Manager.

This technical report is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

For high energy missions in the 1990s, a recently completed Air Force study determined that an advanced pump-fed engine using N_2O_4 and MMH propellants at about the 16700 N (3750 lbF) thrust level best satisfies mission requirements. In order to achieve high performance in a compact envelope, such engines must operate at high chamber pressures 68 to 136 ATM (1000-2000 psia) while maintaining high component efficiencies. The most significant technology advancement required to bring this engine concept to reality is cooling of the combustion chamber under these conditions.

The leading candidate chamber cooling system makes use of a chamber regeneratively cooled with N_2O_4 oxidizer as the coolant. Columbium is one of the candidate materials being considered for the chamber. It has the required physical and thermal properties required for cooling and structural integrity, and is inert to the corrosive N_2O_4. The chamber design approach employs a machined columbium alloy liner with rectangular slots milled ....

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Block 19: onto its exterior, which are subsequently "closed out" with pure columbium using the Chemical Vapor Deposition (CVD) process to enclose and form the coolant passages.

Fabrication issues are concerned with a producibility study of chamber design to enhance CVD processing, evaluation and screening of compatible channel filler materials capable of post-CVD removal, development of filler application methods, and development of CVD coating uniformity on a combustion chamber contour.

Block 18: Etching, Bonds, Chemical Bonds.

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SECTION 1.0 INTRODUCTION

Liquid rocket systems, because of their performance and versatility, are essential to both present and future space operations. To assure our nation's ability to operate effectively in space, new high performance rocket systems are required to transfer spacecraft to geostationary orbit, to inject them into planetary exploration trajectories and to provide spacecraft maneuvering capability.

For high energy missions in the 1990s, a recently completed Air Force study, designated "Advanced Spacecraft Propulsion Design" (Contract F04611-81-C-0046), determined that an advanced pump-fed engine using N_2O_4 and MMH propellants at about the 16700 N (3750 lbf) thrust level best satisfies mission requirements. In order to achieve high performance in a compact envelope, such engines must operate at high chamber pressure (68 to 136 ATM (1000-2000 psia)) while maintaining high component efficiencies. The most significant technology advancement required to bring this engine concept to reality is cooling of the combustion chamber under these conditions.

The leading candidate chamber cooling system makes use of a chamber regeneratively cooled with N_2O_4 oxidizer. Columbium (Niobium) is one of the candidate materials being considered for the chamber. It has the physical and thermal properties required for cooling and structural integrity, and is compatible with the corrosive N_2O_4 in the normal engine operating environment. The chamber design approach employs a machined columbium alloy liner with rectangular slots milled onto its exterior. After filling the slots with a removable filler material, they are "closed out" with pure columbium using the Chemical Vapor Deposition (CVD) process to enclose and form the coolant passages. Fabrication issues are primarily concerned with process equipment and procedure refinements to produce uniform columbium deposits onto the chamber, and improvement of the efficiency of coolant channel filler material installation and removal.

The technology has been addressed in the Columbium Chamber Fabrication Study, Contract F04611-83-C-0057. The objectives of this study are to:

Perform a producibility study of a chamber design permitting attachment of the flanges after CVD coating the slotted liner.

Evaluate and screen channel filler materials compatible with columbium and the process environment, yet capable of post CVD removal.

Develop application techniques for the candidate filler materials.

Demonstrate CVD close-out of slotted, filled, C103 columbium alloy panels and subsequent removal of the filler materials.

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1.0, Introduction (cont.)

    '   Demonstrate the achievement of deposit uniformity on the complex thrust chamber configuration.

The data obtained during the conduct of the program are documented in this report.

SECTION 2.0 CHEMICAL VAPOR DEPOSITION PROCESS

Chemical Vapor Deposition (CVD) has been employed for providing coatings for more than a century, but it is only recently that this technique has left the laboratory to become a production tool in the manufacture of complex refractory metal parts. CVD is a method of plating which relies on the condensation of elements or compounds from the vapor state to form solid structural deposits. Since this is done on an atom-by-atom basis, impurity levels are typically less than 0.1% and densities are 99.9%. The process of chemical vapor deposition utilizes a gaseous compound of the element to be deposited which is flowed over a heated substrate, resulting in thermal decomposition or reduction of the gaseous compound, to form a deposit of the metal onto the substrate. While this process occurs over a wide range of temperatures, the actual temperature chosen is influenced by the required deposition rate, efficiency (percent of material deposited compared to material used), grain size, and bonding characteristics. Low temperature deposition can result in low deposition rate, poor efficiency, small grain and marginal bonding.

The substrate material must be chemically compatible with the deposition gases, withstand the deposition temperature (typically 1150°C (2102 F) for columbium), and have a thermal expansion compatibility such that when the parts are cooled to room temperature the residual thermally induced stresses do not cause cracking or deformation of the coating.

2.1 CVD APPARATUS.

A schematic of the CVD Apparatus is shown in Figure 1. The major elements consist of:

rotating table for supporting the mandrel

reaction chamber for isolating the mandrel in its controlled environment

induction coil for heating the mandrel

sources of chlorine gas, hydrogen, argon, and vacuum

chlorination chamber for the columbium - chlorine reaction to form $CbCl_5$

2.2 CHEMICAL REACTION/VAPOR DEPOSITION

In the Chemical Vapor Deposition apparatus chlorine gas is passed through a container of heated [300°C (572°F)] columbium sheet clippings, forming columbium pentachloride.

$$2 \text{ Cb} + 5Cl_2 \longrightarrow 2CbCl_5$$

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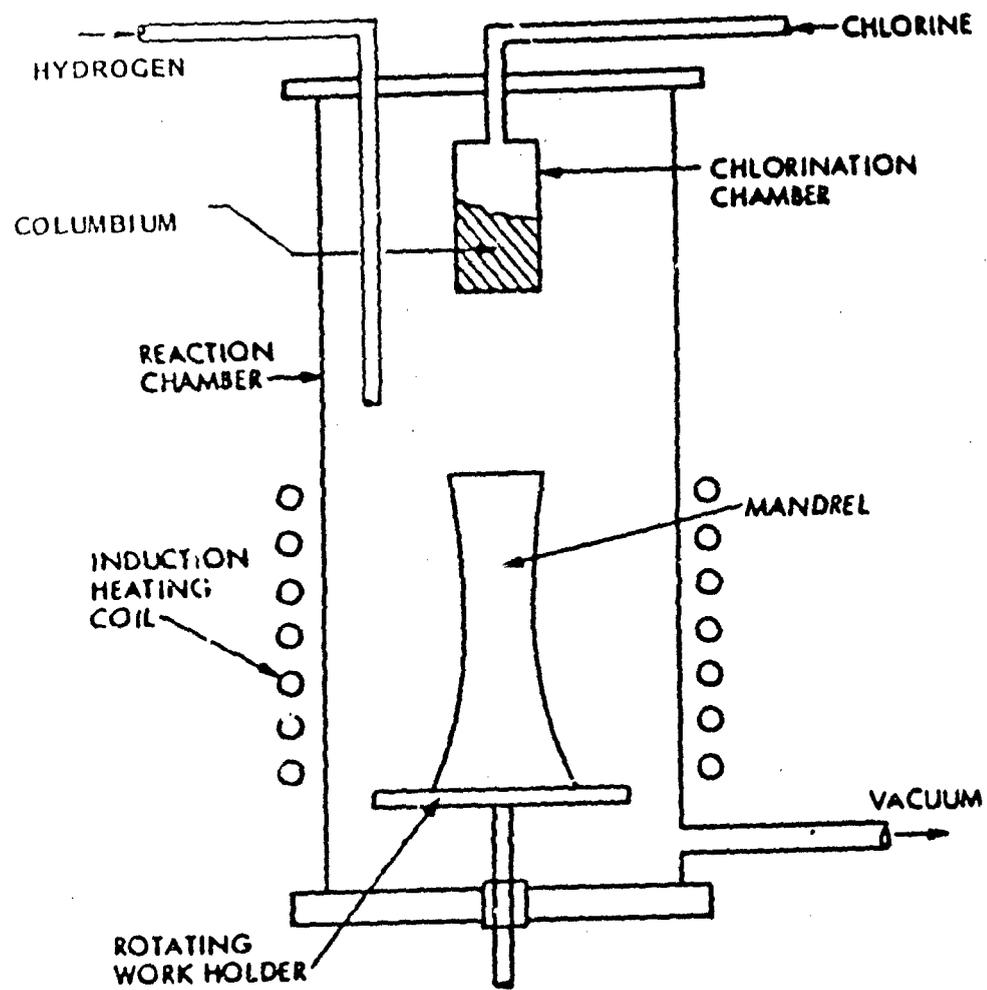
Figure 1. CVD Apparatus Schematic

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2.2, Chemical Reaction/Vapor Deposition (cont.)

The reaction takes place at about 300°C (572°F) but, since the reaction is exothermic, the columbium container need only be initially heated to start the reaction. The heat procuced by the reaction is then sufficient to sustain the reaction.

As this gas mixture passes over the heated substrate [1150 C (2102°F)], hydrogen reduction of the columbium pentachloride takes place, liberating the columbium metal which deposits onto the substrate and releasing HCl gas whicn passes out through the exhaust system.

$$2CbCl_5 \ + \ 5H_2 \xrightarrow{\hspace{1cm} 1150°C \ (2102°F) \hspace{1cm}} 2 \ Cb \ + \ 10HCl$$

(gas)'   (gas)   (solid)   (gas)
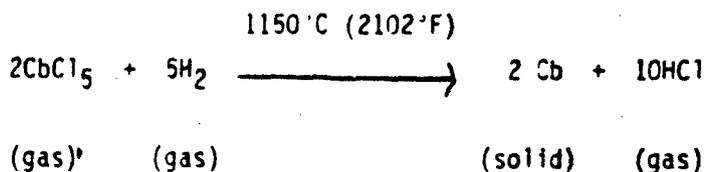
By continuing the process for a sufficient amount of time, a reasonably thick deposition can be achieved.

SECTION 3.0   THRUST CHAMBER DESIGN

Columbium chamber fabrication using the CVD process for coolant channel closeout was first evaluated in a company-sponsored program. Thrust chamber closeout was investigated by machining axial rectangular slots into solid cylindrical C-103 (10% hafnium, 1% titanium, balance columbium) columbium alloy cylinders, filling the slots with molybdenum tubing and "closing out" the slots with CVD columbium. The molybdenum tubing was then etched out. Results were very encouraging: bond strength between the CVD columbium and the C-103 was nearly equal to the strength of the parent material and removal of the slot fillers was successfully demonstrated by flowing nitric acid through the passages to leach out the molybdenum tubing.

Based on these successful results, a thrust chamber of C-103 material was fabricated up to the point of coolant channel preparation for the CVD process. "L" shaped photoetched molybdenum strips were inserted in the channels to provide a CVD deposit over the channel and create flow cavities to assist acid flow.

Following the columbium CVD close-out of the chamber, the coolant channels were flowed with nitric acid to remove the molybdenum filler material. Most channels were opened following this process; however, several channels remained plugged or partially restricted. This was probably due to two causes: 1) deposition of the CVD material into the flow channels via small gaps between the molybdenum filler strip and the channel wall, and 2) plugging from molybdenum oxides formed from nitric acid/molybdenum reactions. The formed oxides were impervious to attack by the nitric acid. Access to the passages for leaching was limited to small diameter holes drilled through the forward and aft flanges of the chamber.

The wide flanges at the forward and aft ends of the chamber presented an additional problem with regard to restriction of the flow of the columbium pentachloride gas over the chamber contour. The combustion chamber is installed in the CVD apparatus in the position labeled "mandrel" in Figure 1. The flanges deflect the downward flowing gas away from the chamber wall with the result that the thickness of deposit at the flange radii was substantially less than in the central region. Baffling and deflector nozzles helped but the results were only fair.

3.1   PRODUCIBILITY DESIGN

A redesign of the flight weight chamber was performed to improve the CVD process capability.   e fundamental change was a redesign of the flanges to permit assembly and w lding to the chamber shell after deposition of the columbium close-out by CVD. This design, Aerojet Drawing No. 1197315, was submitted early in this program under Task 1. A sketch of this design is shown in Figure 2. The design is expected to provide a smoother contour for more uniform flow of the columbium pentachloride gas resulting in a better deposit uniformity.

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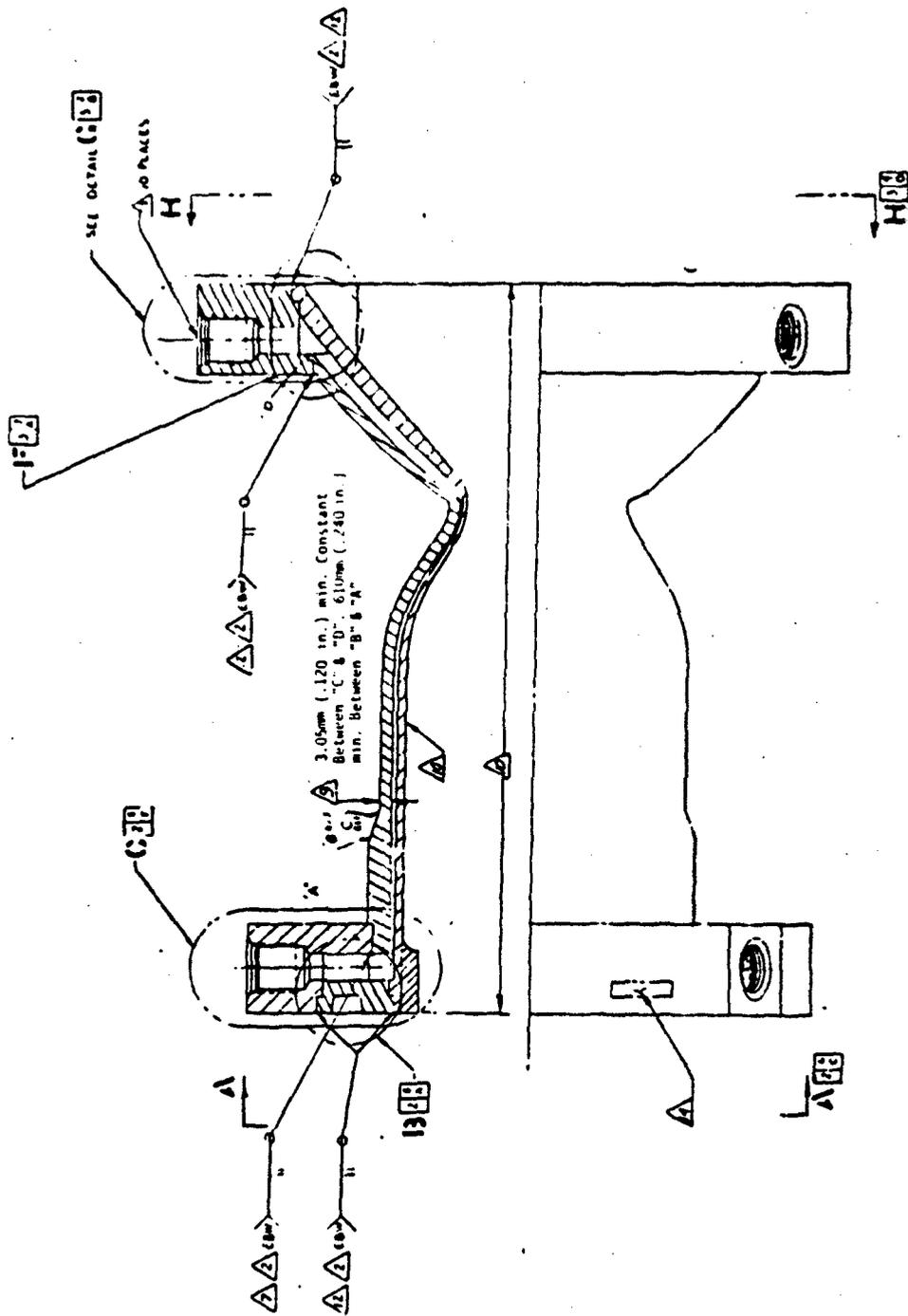
Figure 2. Thrust Chamber Design With Separate Flanges For EB Welding After Columbium Close-Out Deposit

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3.1. Producibility Design (cont.)

The design also permits better access to the ends of the channels for leaching of the protective filler material. Following CVD, the columbium deposit at the ends of the channels can be removed. This circumferential opening will function as the coolant manifold after attachment of the flanges.

3.2 CHANNEL GEOMETRY

The thermal design of the thrust chamber for this relatively low thrust, high pressure engine dictates very small chamber coolant passages, in the order of .76 mm (0.03-in.) to 2.54 mm (0.10-in.) equivalent diameter, depending upon the station along the chamber contour. The chamber channel geometry is of the following general configuration.

| Channel Parameter | Chamber Location | | |
	Barrel	Throat	Exit
Gas Side Wall Thickness, mm (in.)	2.54 (.100)	1.27 (.050)	2.67 (.105)
Channel Depth, mm (in.)	2.03 (.048)	.71 (.028)	3.05 (.120)
Channel Width, mm (in.)	1.27 (.050)	.76 (.030)	2.54 (.100)
Land Width, mm (in.)	1.27 (.050)	.79 (.031)	1.27 (.050)

The continuously variable width and depth channels create additional problems in conforming and retaining filler materials in the coolant channels during the high temperature CVD processing. For this reason, the use of tubing or photoetched strips appeared difficult and costly. Selection of filler materials that will conform and be retained was necessary.

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SECTION 4.0 DEPOSIT UNIFORMITY

A separate task was undertaken to verify that the modified design geo-metry will solve this problem of deposit uniformity. This task was under the cognizance of the CVD subcontractor, Ultramet of Pacoima, Ca. Ultramet specializes in chemical vapor deposition of refractory metals and compounds and performed the columbium vapor deposition in this program.

4.1 SUBSTRATE TEST MATERIAL

The uniformity tests were run on graphite mandrels machined to the external dimensions of the redesigned thrust chamber configuration, without flanges. This contour is shown in Figure 3.

4.2 EXPERIMENTAL RESULTS

The graphite chamber replica was mounted vertically, with the small diameter up, in the quartz reaction chamber. Difficulties were encountered on the initial tests resulting in uneven deposits. This was attributed to non-uniform heating caused by the large difference in diameter between the replica chamber throat and the induction coil.

To improve this uniformity of heating, the induction coil turns were concentrated axially at the throat with wider separation of the coils at the ends. Although some difficulty was experienced in reaching the targeted 1150°C (2102°F), a final run of approximately two hours produced a thickness of .127 mm (0.005 inch) columbium on the barrel section; .107 mm (0.004 inch) at the throat; and a tapering from .107 mm to .178 mm (0.004 inch to 0.007 inch) along the divergent section.

Close-out of the relatively small combustion chamber would employ a quartz reactor chamber conforming more closely to the chamber shape. The quartz chamber would be of a smaller diameter more closely coupled at the barrel section and flare out at the divergent section. This would optimize the coil shape to more evenly heat the combustion chamber.

The smoother chamber contour (without flanges) substantially improved the columbium pentachloride gas flow distribution. However, a large buildup was beginning at the "edge" transition from the conical shape to a cylindrical extension. This "edge" effect can be controlled by intermediate machining between runs or by extension of the chamber contour and parting the excess stock when the ends are prepared for flange attachment. The contoured graphite mandrel, before and after the CVD coating, is shown in Figure 4. Cracking of the deposit at the throat is due to an error in selection of the graphite for the mandrel. The grade of graphite had a mismatch in its coefficient of thermal expansion in relation to columbium.
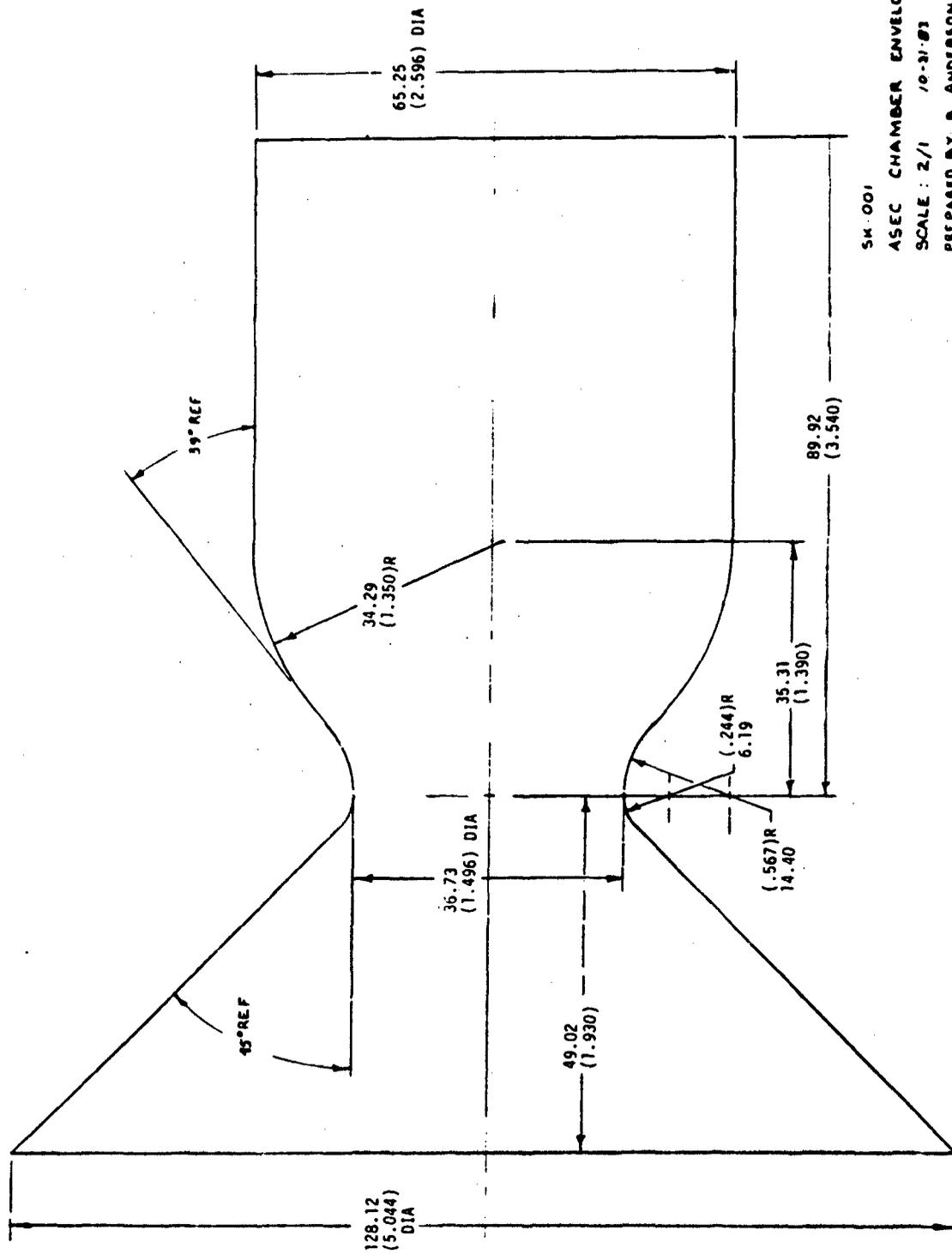
Figure 3. Thrust Chamber Contour
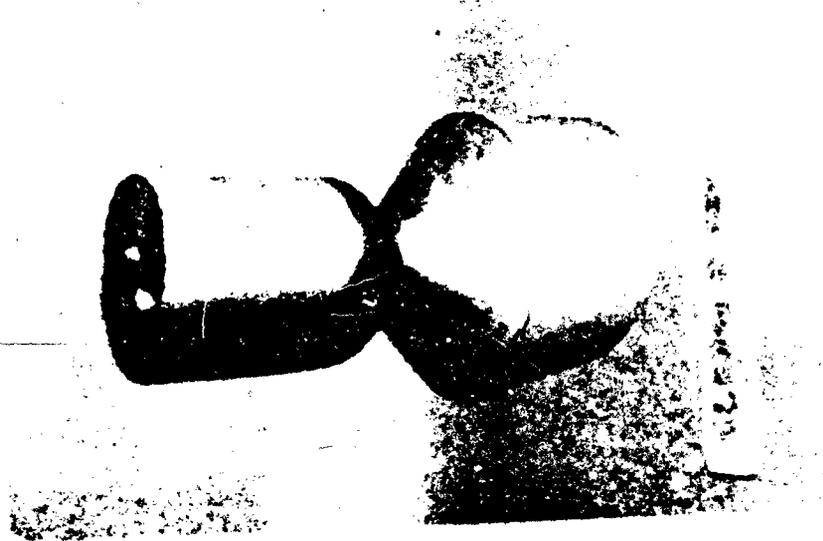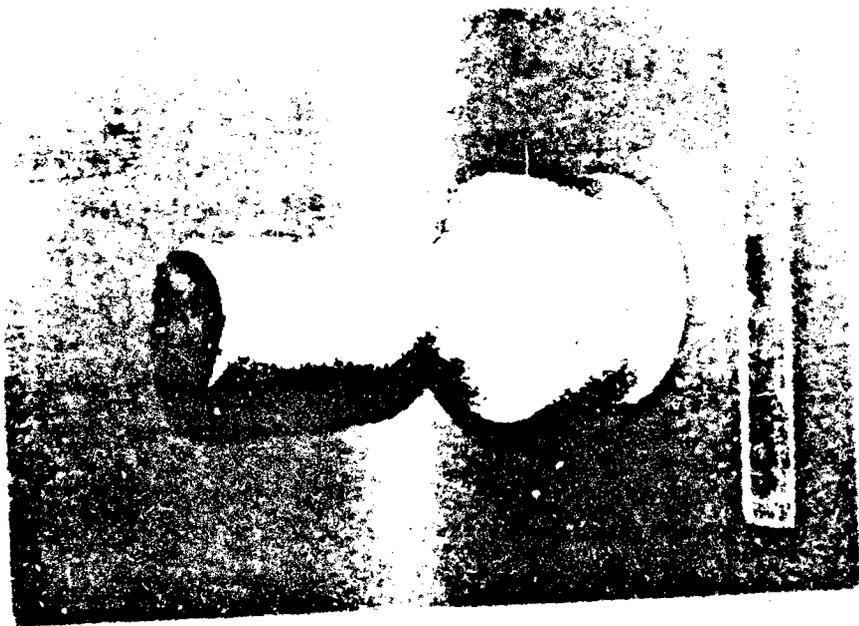
Figure 4. Deposit Uniformity Test. Mandrels of Graphite Machined to the Thrust Chamber Configuration Without Forward and Aft Flanges. Views are Before and After Cb Deposition.

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SECTION 5.0 FILLER MATERIAL SELECTION

Fundamental to the selection of materials to act as protective channel fillers are the following desirable criteria:

Compatible with the columbium alloy substrate

Compatible with the high temperature of the CVD process

Compatible with the reactive gaseous environment in the high temperature reaction chamber

Capable of being applied to small channels of varying width and depth

Capable of being worked as necessary for conformation to the channel cavity

Capable of post-CVD removal by chemical means compatible with the columbium alloy substrate

High temperature salts and metals in wrought and powder forms capable of being "molded" to the three dimensional channel contour became the baseline selection. Table 1 lists the selected candidate filler materials and the processing characteristics of each material/form.

5.1 HIGH TEMPERATURE SALTS

Of the common high temperature salts, soluble in acid or water, three were considered. Calcium oxide (CaO, melting point $2572\,^{\circ}C$ ($4662\,^{\circ}F$)), barium oxide (BaO, melting point $1923\,^{\circ}C$ ($3493\,^{\circ}F$)), and potassium orthophosphate (K_3PO_4, melting point $1340\,^{\circ}C$ ($2444\,^{\circ}F$)), all have a melting point well above the stated typical $1150\,^{\circ}C$ ($2102\,^{\circ}F$) CVD temperature for columbium deposition. Initial difficulties on application (discussed below) and the greater hygroscopic nature of CaO and BaO resulted in the selection of the water soluble K_3PO_4 salt. The latter is considered to be stable at high temperature.

With induction heating used for the CVD process, improvement of the inductance of salt by addition of metal powders was also considered. It was expected that the presence of the water soluble salt would accelerate the leaching of a metal powder.

5.2 COPPER

Copper is a desirable candidate because of ease of dissolution with nitric acid. However, the melting point of copper [$1083\,^{\circ}C$ ($1981\,^{\circ}F$)] is well below the nominal CVD/Cb temperature conventionally employed. This requires, therefore, a lower process temperature, i.e., below the melting point of

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TABLE 1. SELECTED FILLER CANDIDATES

Filler Materials	Form	Filler Temp. Limit °C (°F)	Reactions with Substrate	Binder	Application Method	Cure/ Sinter Cycle °C (°F)	Etchant/ Solvent
Molybdenum	Foil	2620 (4748)	None	None	Mech. Conform.	None	HNO_3;H_2SO_4
	Powder	2620 (4748)	None	Acrylic	Molded	1200 (2192) Vac.	HNO_3;H_2SO_4
Iron	Powder	1372 (2502)	Cb-Fe Inter-metallic, Eutectic	Acrylic	Molded Slurry	1200 (2192) Vac.	HNO_3
Mo/Fe Mix	Powder	1372 (2502)	Cb-Fe Inter-metallic, Eutectic	Acrylic	Molded Slurry	1200 (2192) Vac.	HNO_3
Copper	Wire/Tubing	1083 (1981)	Cu-Hf Eutectic*(?)	None	Mech. Conform.	None	HNO_3
	Powder	1083 (1981)	Cu-Hf Eutectic*(?)	Acrylic	Molded Slurry	650 (1202) Vac.	HNO_3
	Powder	1083 (1981)	Cu-Hf Eutectic*(?)	K_3PO_4	Molded Slurry	70 (158) 158 (350) 350 (662)	H_2O/HNO_3
Nickel	Powder	1100 (2012)	Cb-Ni Eutectic	Acrylic	Molded Slurry	650 (1202) Vac.	HNO_3
K_3PO_4	Water Solution	1340 (2444)	None	K_3PO_4	Molded Slurry	70 (158) 350 (662)	H_2O
	Solution with Al_2O_3	1340 (2444)	None	K_3PO_4	Molded Slurry	70 (158) 350 (662)	H_2O

*Observed with molten copper contact.

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5.2, Copper (cont.)

copper. A low deposition rate is anticipated as well as a potentially lower
bond strength. The approach would be to deposit approximately .25 mm (0.010-
in.) thick columbium. Following this, the copper would be chemically removed
and the closed-out part subsequently recycled at the higher 1150°C (2102°F)
conventional temperature to more efficiently build up the required columbium
coating thickness.

Copper is metallurgically compatible with columbium in that it forms no
intermetallic or low melting eutectic phases. However, brazing studies at ATC
have shown a detrimental reaction between molten copper and C103 alloy. (This
was not the case with FS85 alloy.) Extensive grain boundary diffusion of
copper into the C103 substrate suggests a Cu-Hf reaction (C103 contains 10%
hafnium). However, short term diffusion of copper from the solid state is not
anticipated to be detrimental.

5.3   MOLYBDENUM

Experience with chemical dissolution of wrought molybdenum fillers has
been poor. It is still considered for evaluation because of its solid
solubility with columbium and high melting point. Columbium and molybdenum
form a solid solution because they have the same crystal structure, a close
atomic ratio, and a similar electronic structure. They form a single phase
for all compositions of the two elements. Wrought and moldable powder forms
were considered in conjunction with techniques to produce "in situ" cavities
enabling acid flow to accelerate leaching.

5.4   IRON

The ready solubility of iron in nitric acid and its relatively high
melting point 1538 C (2800 F) make iron a good filler material candidate.
Unfortunately, iron forms three intermetallic phases with columbium below
1200°C: Cb_2Fe_2, $Cb_{19}Fe_{21}$, and $CbFe_2$. At 1150°C (2102°F) the solubility of
iron in columbium is approximately 4 atomic percent (a/o). The most likely
phase to form in a limited contact situation, i.e., soild iron particles in
contact with columbium, is the Cb_2Fe_2, which is 40 a/o iron. Therefore,
unless the contact is at very high temperature or for a long time, the iron
diffusion will be very limited. This should confine any intermetallic
formation to only the point of contact.

In reviewing eutectic formations with C103 alloy, a Cb-Fe eutectic (89
a/o Fe-11 a/o Cb) forms at 1372°C (2502°F). Hafnium also reacts with iron.
The Fe-Hf phase diagram shows the formation of two intermetallic compounds,
$HfFe_2$ and Hf_2Fe and two eutectics (melting points of 1350°C (2462°F) at 8 a/o
Hf and 1300°C (2372°F) at 64 a/o Hf). However, CVD of columbium is normally
performed well below these temperatures.

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5.4, Iron (cont.)

As with the copper, the high temperature exposure of the iron in the channels will be limited. After an initial columbium deposit of .20 mm to .25 mm (0.008 to 0.010 inch) thickness over the iron filled channels, the iron will be removed before final buildup of deposit thickness.

Also, mixing of molybdenum and iron powders is a consideration to minimize potential iron diffusion and perhaps provide better leaching than with just pure molybdenum. Intermetallic formation (Mo_2Fe_3) was also considered.

5.5 NICKEL

Nickel was considered as an intermediate selection between iron and molybdenum. More difficult to remove than iron but easier than molybdenum, it behaves similar to iron in reaction with columbium. Two intermetallic phases are reported (CbNi and CbNi$_3$). Of greater concern is a Ni-Cb eutectic phase which melts at approximately 1100°C (2012°F). Similar 1100°C (2012°F) and 1200°C (2192°F) eutectics phases are potential hazards with nickel-hafnium reactions. Because of these formations possible at the processing temperature, nickel appears to be metallurgically impractical.

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SECTION 6.0 EXPERIMENTAL APPROACH

A slotted panel specimen design was used as a cost-effective method to demonstrate methods of application of the filler materials and their removal subsequent to CVD of a columbium close-out. C103 columbium alloy plate, procured to Aeronautical Materials Specification (SAE) -- AMS 7852, was used for the substrate material. This alloy had been selected by Aerojet for the Advanced Space Engine Components (ASEC) chamber design. The CVD processing of these filled panels was performed on an octagonal carousel/susceptor fabricated from graphite. This cylindrical shape provided a simulation of the chamber configuration which is rotated in the quartz reaction chamber.

6.1 SLOTTED PANELS

Panel configuration is shown in Figure 5. Standard cutter sizes were selected to mill the square channels with dimensions of .81mm (0.032 inch), 1.57 mm (0.062 inch), and 2.39 mm (0.094 inch) wide. The land width between channels was standardized at 1.77 mm (0.050 inch). The channel sizes are characteristic of the variable width channels of the flight chamber design; a photograph of a slotted panel is shown in Figure 6.

The holes at the ends of the large channels were also used to leach out the filler. After CVD coating with columbium, the panels were sectioned across the channels, 50.8 mm (2 inch) in from the end of the panel with the extended length 2.39 mm (0.094 inch) channels. This provided a 76.2 mm (3 inch) section for leaching experiments with the adjacent piece mounted for metallurgical evaluation.

6.2 CAROUSEL FIXTURE

Flow direction of the reactive $CbCl_5$ gas is important to deposit uniformity. For this reason, a graphite fixture was fabricated to retain the panels in a near vertical orientation. Octagonal in shape, the fixture permitted eight test coupons for each of the three planned carousel runs.

The sequence of views in Figure 7 show the carousel fixture with panels in place for the first CVD run. The graphite fixture is supported on a rotating graphite shaft. Assembly of the fixture is shown before placement of the reaction chamber and also assembled with the induction coil.

6.3 FILLER APPLICATION METHODS

The physical and chemical properties of filler materials and the compatibility with the thermal and the reactive gas environment during CVD were discussed above. Equally important is the ability to apply the selected materials to small channels of variable width and depth. In situ molding of the fillers to the channels appeared most desirable. Techniques such as plating, electroforming, spraying, forming, powder metallurgy and slurry molding were considered.

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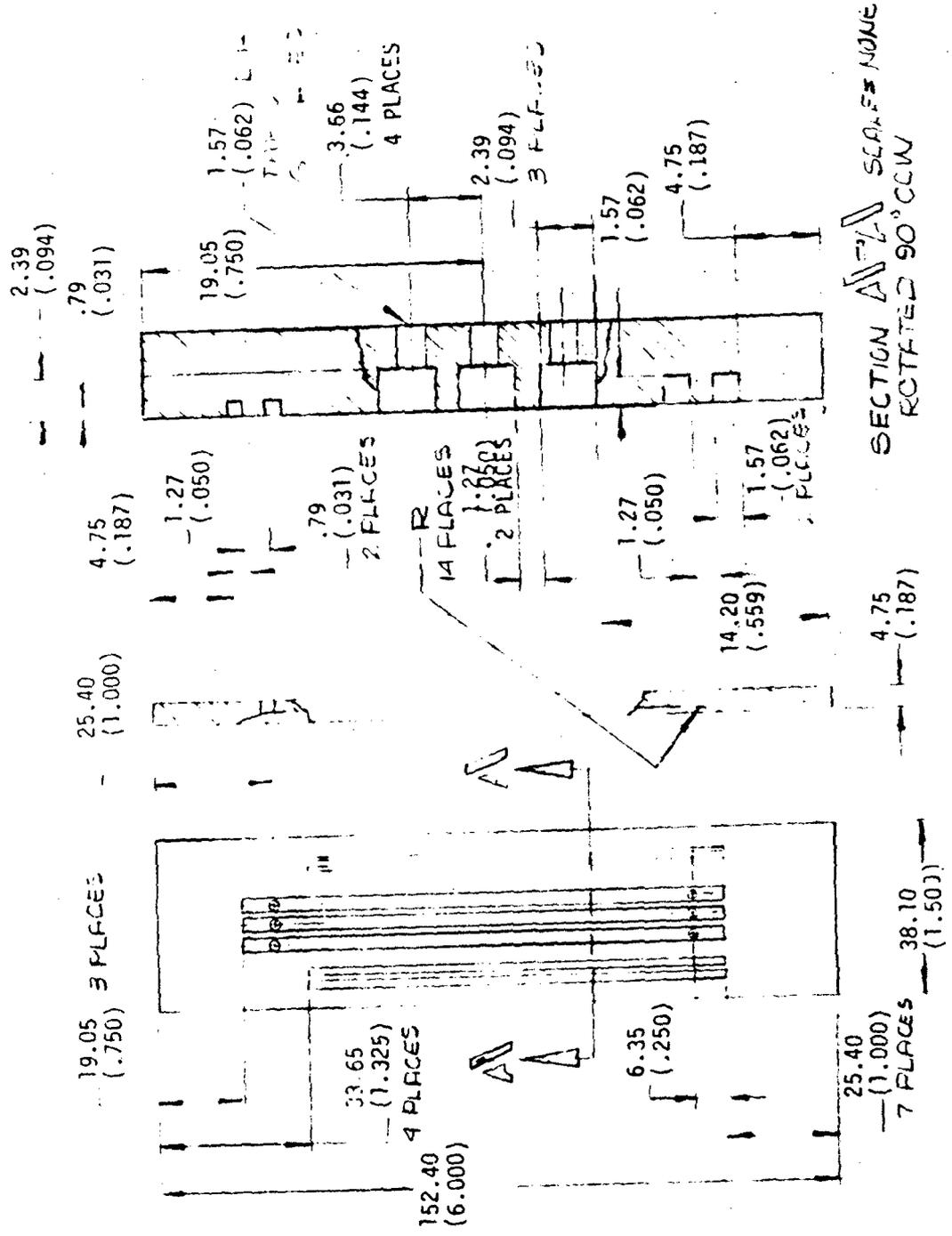
Figure 5.   Slotted Test Panel Design

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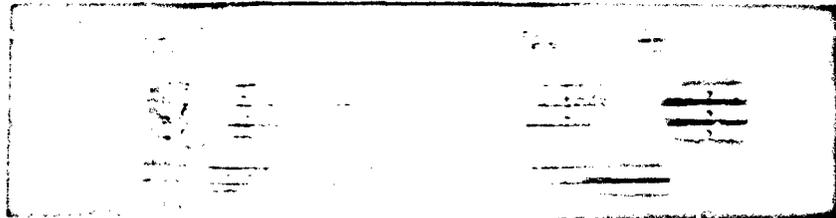
Figure 6.   C103 Test Panel with Machined Channels .81mm (0.032 in.),
1.57mm (0.062 in.), and 2.39mm (0.094 in.) Square
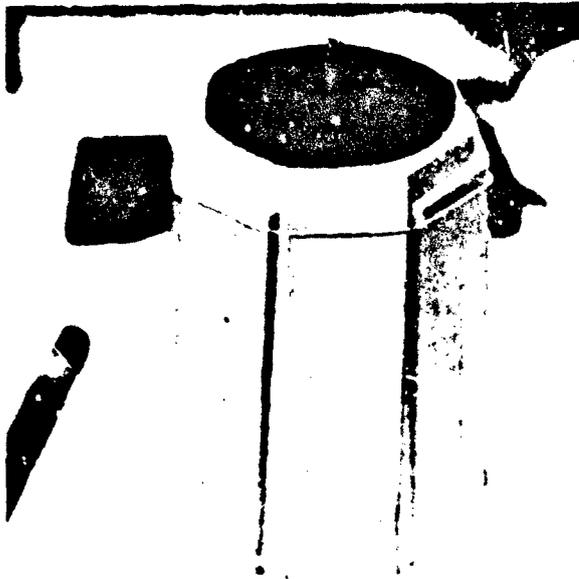
Panels Mounted on Fixture After First
CVD Run
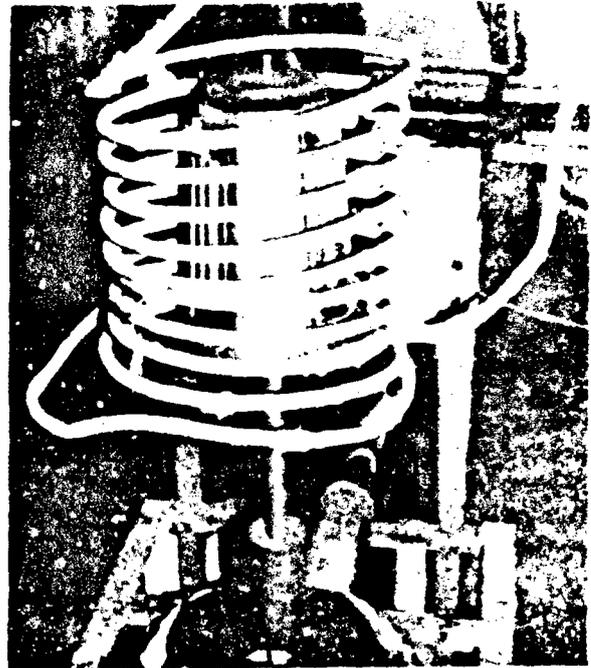
Rotating Carousel Set-up
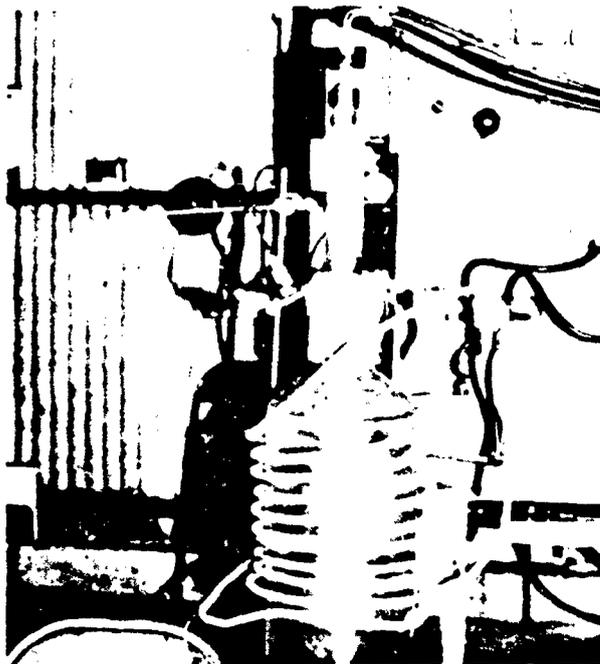
Quartz Reaction Chamber in Place

Induction Heated Carousel - First CVD Run

Figure 7. Graphite Carousel Fixtures Eight Slotted Panels for CVD
Processing

6.3, Filler Application Methods (cont.)

6.3.1 High Temperature Salt Filler

Water soluble potassium orthophosphate, selected for evaluation, was mixed with water as the carrier. As such, the salt was not moldable. The mixture would agglomerate and proved difficult to trowel. Baking experiments resulted in a large amount of shrinkage. Aluminum oxide powder was added to reduce the shrinkage in the channels. Mixing the fine aluminum oxide powder with the salt slurry also smoothed out the flow. A mixture of 50% Al_2O_3 in the salt provided optimum results and this basic mixture was used for all salt related tests.

Water was removed in a two step bake cycle. Overnite baking at 70°C (158°F) was followed by a one hour exposure at 350°C (662°F) to drive out the water of hydration. Thermogravimetric analysis, Figure 8, shows all water of hydration is removed at 200 C (392°F). Although not as hygroscopic as the other salts considered, baked panels had to be stored and transported under desiccant. Cleaning excess basic salt filler from the lands was easily accomplished.

6.3.2 Metal Filler

The copper, molybdenum, and iron powders used, all -325 mesh, were of average micron size 20u, 15u, and 15u, respectively. Copper powder of 50u to 150 was also used.

These powders, in some cases compacted over cavity formers or cores to provide a flow passage for the leaching media, were to be the base line approach. Pressing and sintering the powders over tubing of the selected metal would require substantial investment in tooling and processing costs. Tubing of desired diameter required special order and extended delivery. A simpler approach employed acrylic cement as a carrier for the powders and permitted molding of the powder in the channels. The acrylic cement is one used in brazing with powdered brazing alloys. The acrylic vaporizes at about 450°C (842°F) leaving a small carbon residue (iron powder-acrylic slurry analyzed 0.12%C after sintering at 1150°C (2102°F)).

Prior experience with molybdenum dictated a need for a leaching flow cavity if removal was to be successful. Small diameter plastic tubing, nylon line, cotton cording, and molybdenum tubing were placed in the channels and the powder slurry molded over them. The molded materials were sintered in place leaving a cavity with a small amount of residue. Wires, coated with various release agents were also molded in place and were removed after air drying the powder slurry. This method did not prove practical considering the complexities of applying it to an actual chamber configuration.

Sample: K3PO4/ALOX50/50
Size: 20.45 mg
Rate: 20 C/MIN
Program: General Analysis V1.0

Date: 15-Dec-83   Time: 10:04:04
File: CFAB.07 MISC. TGA DATA NO.
Operator: JAC N 50 CC/MIN
Plotted: 15-Dec-83   12:37:56

Temperature (°C)

Temperature (°F)

Weight (%)

DuPont 1090
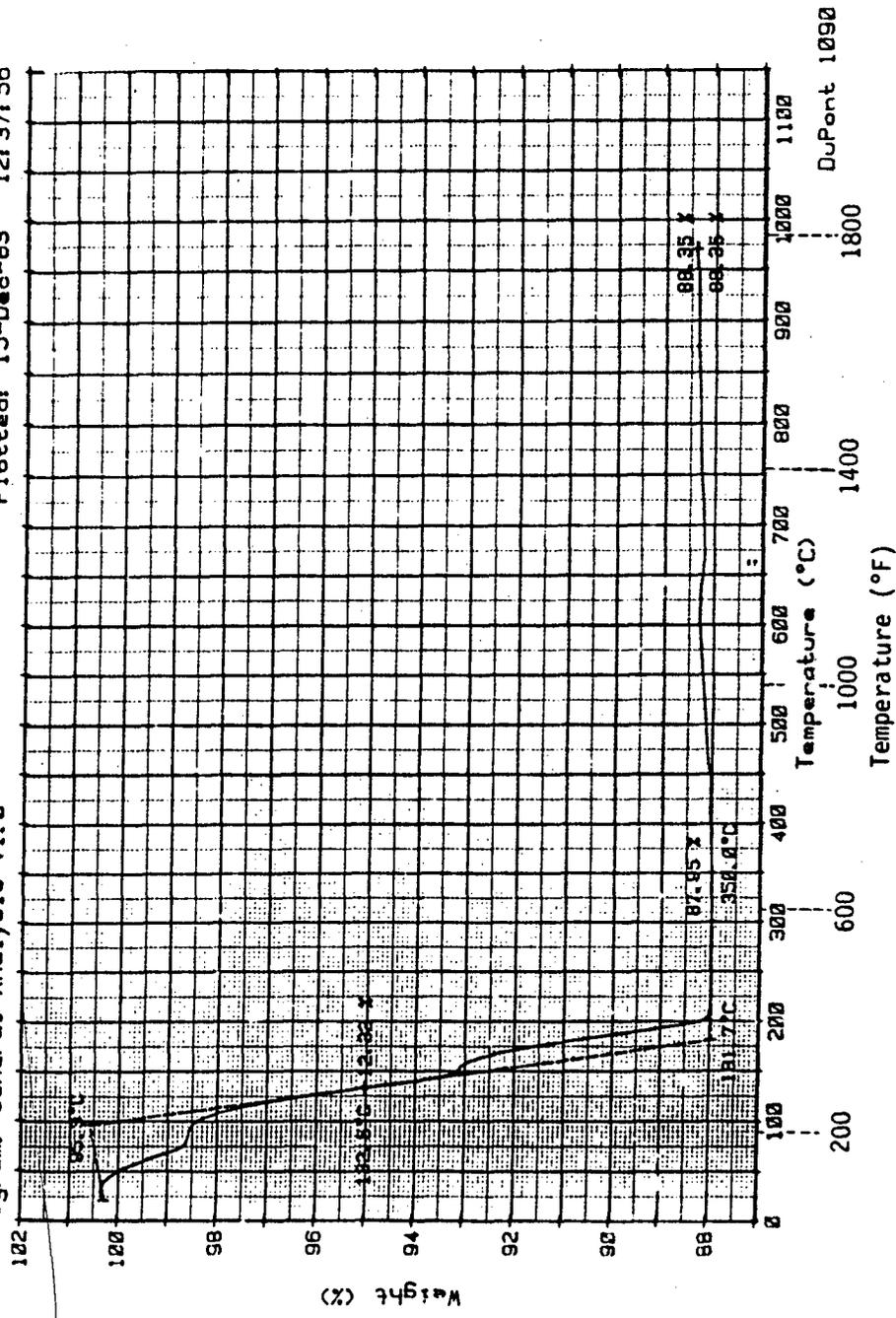
Figure 8.   Thermogravimetric Results of K_3PO_4/Al_2O_3 Basic Salt Mixture
Shows All Water of Hydration Removed at 200°C.

6.3, Filler Application Methods (cont.)

Such cavity formers were not considered necessary for copper with its excellent dissolution in nitric acid. Wrought copper forms, tubing, foil, and wire of various sizes were formed in the channels. Although the copper is quite malleable, the soft (Rockwell B 80/85) columbium alloy lands sustained damage in attempting to obtain full channel conformation of the wrought material.

Copper powder molded with the acrylic carrier in the channels was sintered at 1000°C (1832°F) in vacuum. This sintering was performed with the panel in the vertical position to assess retention of the powder. The powder was retained in the channels and the excess copper could be filed and sanded even with the lands.

Plastic tubing was used in some experiments with iron powder but subsequent sintering tests on the iron filled channels dispelled any need for extraneous cavity formers. Due to the large difference in the coefficient of thermal expansion of iron in relation to the columbium substrate, a shrinkage cavity was created along the sides of the channels providing a continuous flow passage for the leaching acid.

Removing the excess material from the lands was done by filling, hand sanding, and, for the panels of the third CVD run, by belt sanding. Machine milling of the lands should be used for chamber fabrication.

SECTION 7.0 CVD CAROUSEL RUNS

7.1 LOW TEMPERATURE TESTS

CVD processing at a temperature below the melting point of copper (1083°C (1981°F)) required preliminary low temperature screening runs. The subcontractor first used 38 mm (1.5 inch) diameter graphite discs to observe columbium deposit rates at optically read temperatures as low as 950°C (1742°F). It appeared that even deposits were being obtained but at low rates estimated at less than .025 mm (0.001 inch) per hour.

In order to obtain a rate of deposit on columbium, screening tests were run on 38 mm (1.5 inch) diameter slotted discs. These discs were cut from the slotted panels and the corners rounded. Four discs, filled with two salt mixtures, copper, and iron, were prepared for close-out.

7.2 CVD RUN NO. 1

The initial carousel run was to be conducted at a low temperature to evaluate copper fillers and an initial evaluation of the basic salt. A temperature lag in the salt containing channels of the discs in the screening run was significant because of its low inductance. Even though not in good electrical contact, it was decided to mix both copper powder and iron powder with the basic salt to see if the inductance could be improved. Five copper only containing panels and three with salt as shown in Table 2 were assembled on the carousel for the first run.

7.3 CVD RUN NO. 2

The higher temperature metals, iron and molybdenum were selected for the second run and a deposit of .30 mm to .38 mm (0.012 to 0.015 inch) thickness of columbium was targeted. This run was to be performed at the conventional columbium deposit temperature of 1150°C (2102°F).

The fillers and cavity forming experiments are described in Table 3. Two molybdenum specimens were prepared with the acrylic slurry. Only the central slot (2.39 mm (0.094 inch)) contained a small diameter PVC tube to be evaluated as a cavity former to aid in dissolution of the molybdenum. Two iron/acrylic mix panels were also made with PVC tubing. Two panels contained iron/acrylic only and two others contained, in addition, a slurry coating of aluminum oxide powder. The aluminum oxide powder was mixed with the acrylic cement and "slip-cast" onto the channel surfaces leaving a thin coating. The acrylic coating was then dried and the iron slurry molded into the coated channels. This was done to evaluate its effect as a protective barrier to minimize potential reaction between the iron and columbium.

23

TABLE 2. CVD RUN 1 - PANEL SPECIMENS

1000°C (1832°F) for Copper

Panel No.	Filler Material	Thermal Treatment
3	K_3PO_4/Al_2O_3*	70°C (158°F) + 350°C (662°F) + 650°C (1202°F)(Vac)
6	55% Fe/Bal. Basic Salt	70°C (158°F) + 350°C (662°F) + 650°C (1202°F) (Vac)
7	34% Cu/Bal. Basic Salt	70°C (158°F) + 350°C (662°F) + 650°C (1202°F) (Vac)
8, 9, 15	Cu/Acrylic (-320 Mesh)	650°C (1202°F) (Vac)
11, 12	Cu/Acrylic	650°C (1202°F) (Vac)

*Basic Salt Mixture - -50% Each.

TABLE 3. CVD RUN 2 - PANEL SPECIMENS

Panel No.	Filler Material*	Cavity Former
2	Mo/Fe/Acrylic (2/3 Mo + 1/3 Fe)	None
5	Fe/Acrylic	PVC Tubing .76 mm (0.030") O.D. in 1.52 mm (0.060") & 2.39 mm (0.094") slots
13, 14	Fe/Acrylic	None
16	Fe/Acrylic	Al_2O_3 Coating on Channel Surfaces
17	Fe/Acrylic	Al_2O_3 Coating Plus PVC Tubing .76 mm (0.030") O.D. in .81 mm (0.032") & 1.57 mm (0.062") slots 1.52 mm (0.060") O.D. in 2.39 mm (0.094") slots
18	Mo/Acrylic	PVC Tubing .76 mm (0.030") O.D. in Center 2.39 mm (0.094") slots
19	Mo/Acrylic	PVC Tubing 1.57 mm (0.060") O.D. in Center 2.39 mm (.094") slot

*All specimens sintered at 1150°C (2102°F) in vacuum.

7.3, CVD Run No. 2 (cont.)

The final panel in this series was made up of a 2/3 to 1/3 mixture of molybdenum to iron. This mixture is near the thermal expansion of columbium. These panels were sintered in vacuum at CVD temperature of 1150°C (2102°F). With the thermal expansion of iron much greater than columbium, there was concern that after vaporizing the acrylic binder the iron filler might be expelled. The Mo-Fe mixture was intended as a gage of this effect.

7.4   CVD RUN NO. 3

The filler material selections for this run were made after evaluation of the results of run No. 2. The preliminary leaching tests showed the iron to be readily removed from the channels and the molybdenum still difficult even with the cavities in tne central channels of panel Nos. 18 and 19.

A verification of the results on the iron/acrylic in run No. 2 was planned. Replicates of the iron/acrylic (23, 27) and a modified iron/acrylic (24, 26) were made. The latter two differed only in that a molybdenum slurry was slip-coat on the walls of the channels and dried before filling with tne iron acrylic. (This was an attempt, similar to the Al_2O_3 slip-coat in run 2, to provide an interdicting barrier between the iron and columbium.)

A higher iron-content iron/molybdenum mixture (80:20) was placed in panel 25 to assess possible improvement in the leaching rate.

Molybdenum powder slurry was molded over two additional cavity formers. One was .61 mm (0.024 inch) diameter molybdenum tubing. The tubing is somewhat brittle and would present problems in forming to the chamber shape and perhaps, retention in the channels. However, this was attempted in the flat panels to compare with prior experience in leaching only molybdenum. The second molybdenum/acrylic panel was molded over cotton cording. The cellulose, when sintered at elevated temperature, should leave only a small amount of residual carbon.

Panel 13 was the iron filled panel coated with .35 mm (0.014 inch) columbium on the second CVD run. The three large channels had been leached to remove the iron. The smaller channels still contained iron. The identification and nature of all these panels is given in Table 4.

TABLE 4. CVD RUN #3 - PANEL SPECIMENS

Panel No.	Filler Material*	Cavity Former
4	Mo/Acrylic	.61 mm (0.024") O.D. x .25mm (0.010") I.D. Mo Tubing 2 each in 2.39 mm (0.094") slots 1 each in 1.57 mm (0.062") slots None in .81 mm (0.032") slots
22	Mo/Acrylic	Cotton Cording .91 mm (0.036") Dia in 2.39 mm (0.094") slots .43 mm (0.017" Dia in 1.57 mm (.062") & .81 mm (0.032") slots
23, 27	Fe/Acrylic	None
24, 26	Fe/Acrylic Channel Surface	Slip Cast Mo/Acrylic Coating
25	Fe/Mo/Acrylic 80% Fe + 20% Mo	None
13	CVD Coated in Run 2. (Fe Filler Leached -- out of 2.39 mm (0.094") slots	

*All specimens sintered at 1150°C (2102°F) in vacuum (Vertical Position).

SECTION 8.0 CVD TEST RESULTS

The copper specimens of both the low temperature screening and the first carousel run were coated with a deposit of columbium and apppeared to be satisfactory. However, subsequent examination showed that the copper had melted and in some cases partially resolidified and remained in the channels.

Temperature is measured by an optical pyrometer and manual adjustments are made to the RF generator to control temperature within the desired range. However, the temperature reading is influenced by the clarity of the radiating source. When the $CbCl_5$ salt begins flowing within the reaction chamber, it "fogs" over the induction heated workpiece. A good deal of control appears to be vested in the experience of the operator.

The second run with iron and molybdenum produced specimens with .35 mm (0.014 inch) thick columbium to be used for leaching and metallographic evalu- ition. The third carousel run also had a temperature overrun. A temperature excursion, possibly coupled with some iron reaction (possibly formation of a Cb-Fe eutectic at 1372 C (2502 F)), resulted in the melting of the iron in the panels.

The CVD runs were begun witn a vacuum check of the system and a five cycle evaluation and back-fill with argon prior to heating the workpiece to the CVD temperature in an argon atmosphere. Flow of the chlorine gas into the chlorination chamber and hydrogen gas into the reaction work zone is started when the deposition temperature is stabilized. The system operates at a negative pressure to preclude the escape of chlorine gas into the work area. This negative pressure appears to be a possible cause of air leakage into the chamber. Surface oxygen contamination of the C103 columbium alloy was evident in all metallographic sections.

8.1 LOW TEMPERATURE DEPOSIT TESTING

The objective of this test was to determine if columbium could be deposited below the melting point of copper (1083°C (1981°F)). Initial tests on the rotating graphite discs were performed from 950°C to 1050°C (1742°F to 1922°F). All temperatures are reported optical pyrometer readings. Columbium deposited at a decreasing rate with lowering temperature. Thickness measurements were made on slotted columbium discs filled with copper, salt, and iron. Three runs were made with the following deposit rates for the indicated temperature range:

1. 1025°C (1877°F) to 1050°C (1922°F): 0.025 mm (0.001 inch) Cb/hour

2. 985°C (1805°F) to 1000°C (1832°F): 0.007/0.010 mm (.0003/.0004 inch) Cb/hour

3. 950°C (1742°F) to 975°C (1787°F): 0.0025 mm (.0001 inch) Cb/hour

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8.1, Low Temperature Deposit Testing (cont.)

Figure 9 is the copper filled disc showing the CVD columbium over the channels after the 75 minute run. Initial examination indicated proper coating with some blue/straw discoloration due to oxide formation. However, sectioning of the disc normal to the channels, disclosed that the copper had melted after the deposition of the columbium had started. Only one large channel retained the melted and resolidified copper powder. The C103 discs were resting on a graphite support. This fixture, apparently hotter than the specimen, possibly overheated the specimen by conduction from the underside.

The upper view of Figure 10 is a photomicrograph at the 2.39 mm (0.094 inch) land showing a 0.5 mm (0.02 inch) thickness of columbium and copper at the substrate/deposit interface. The reaction zone (marked "0") is due to oxygen diffusion. The 0.5 mm (0.02 inch) deep zone has a hardness of Rockwell B (R_B) 36. The .20 mm (0.008 inch) thick pure columbium deposit is very soft, R_B 32 to 56, and the substrate C103, R_B 81.

The lower view is a section of channel which had been filled with the basic salt mixture (K_3PO_4/Al_2O_3; 50% each). The bond is poor. Outgassing of the salt was observed during heat-up. The columbium deposit over the salt is 0.001 inch less in thickness than that over the adjacent substrate land. This is due to a lower deposition temperature caused by the poorer induction heating response of the salt filled channels. The "lace work" over the leached channel is where the columbium penetrated the salt/Al_2O_3 powder surface.

8.2 CVD RUN NO. 1

Panels 12 and 15 shown in Figure 11 are typical of the results obtained for the five copper filled panels. The "as deposited" panels had some shrink-age cracks in the coating. The copper in all panels, including No. 7 (copper in salt mixture), melted and partially resolidified. The temperature excursion appears to be even greater than that experienced on the screening run with the discs. This is evidenced by copper infiltration into the C103 grain boundaries across the 1.27 mm (0.050 inch) thick land. The surface reaction zone depth, well defined by the etchant (H_2SO_4, HF, H_2O_2) is 0.5 mm (0.02 inch) deep. It is apparent that the optical pyrometer readings were low by at least 100 C (212°F).

The salt containing panels Nos. 3 and 6 are seen in Figure 12. The baking and transporting under desiccant was apparently not sufficient to preclude moisture and air entrapment. On heating to the 950°C (1742°F) to 1000 C (1832°F) CVD temperature, outgassing was observed. Subsequently a "linear expulsion" of salt appeared following the centerline of the larger channels. This resulted in a thin columbium "fin" formation. The oxide layer was three times (.15 mm (0.006 inch)) the depth of that observed on the copper filled panels in this same carousel run. The reaction zone was very brittle

29
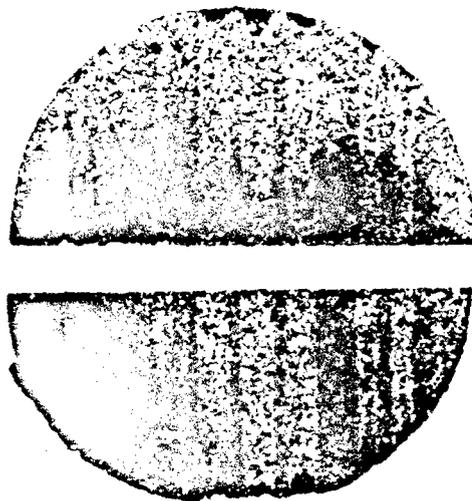
Mag 2X

Slotted Disc After CVD and Sectioning
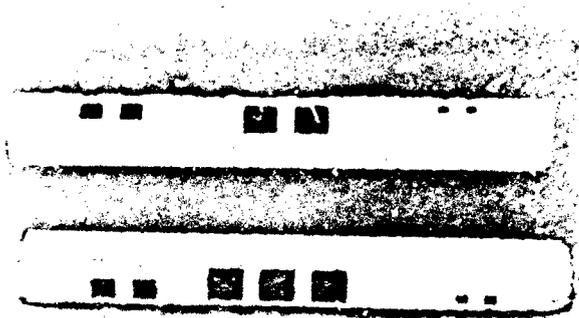
Mag 2X

Top Section is Condition After CVD.
Bottom Section is After Etching.

Figure 9.   Slotted Discs Used For Screening Test

30
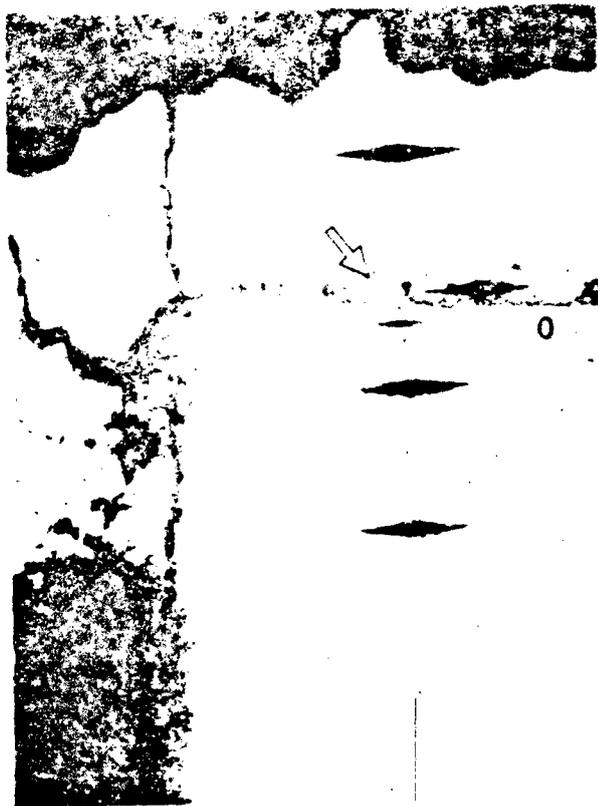
Mag 125X

Copper Melted and Resolidified on Land
(Arrow)
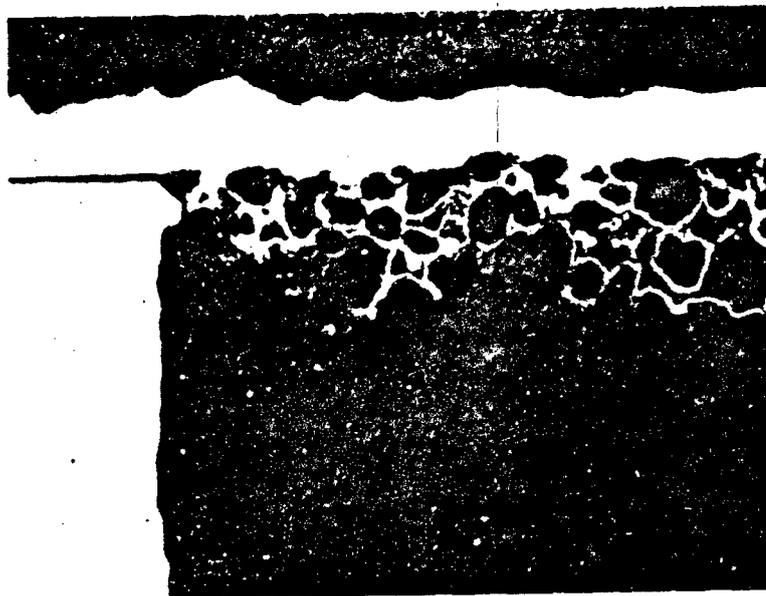
Mag 100X

Basic Salt Dissolved Leaving Cb "Network"

Figure 10. Photomicrographs of CVD Screening Run Specimens of
Copper (Top) and Salt (Bottom) Filled Channels

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Panels 12 & 15 - (Copper) After
Columbium Deposit

Mag 20X
Panel 12 - 1.57mm (.062 in.)
Channels, Copper Melted and
Resolidified

Mag 100X
Panel 12 - 1.57mm (.062 in.)
Channel, CVD Cb Deposit
.05mm (0.002 in.) (Arrow)
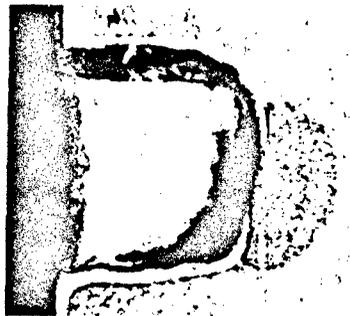
Mag 63X
Panel 8 - .81mm (0.032 in.)
Channel, Molten Copper
Infiltration Into Substrate

Mag 63X
Panel 8 - Land at 2.39mm (.094 in.)
Channel, Surface Oxide Zone
.05mm (0.002 in.) Deep

Figure 11. Typical Sections of Copper Filled Channels Which Melted During
First CVD Carousel Run

Mag 50X

Panel 6 - .81mm (.032 in.) Channel
Brittle Oxygen Diffusion Zone
.15mm (0.006 in.) Deep

Panel 6 - Fe/Salt filled
Channels Also Exfoliated
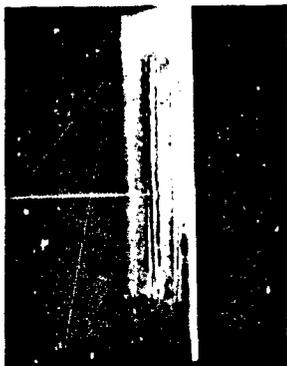
Panel 3 - Basic Salt, CVD
on First Run, Linear Salt
"Expulsion"

Mag 80X

Panel 6 - Sharp Zone Defined By
Etchant. Cb Deposit < .025mm
(0.001 in.), No Bond

Rockwell
Hardness

R_c 22
46_{51}50
R_b 80
85

R_b 79

Mag 125X

Panel 3 - Brittle Zone Exhibited
Hardness to R_c51

Figure 12.   CVD Run 1 with Basic Salt and Salt-Iron Mixture

33

8.2. CVD Run No. 1 (cont.)

(Rc 51) with intergranular cracking at the corners of the lands. There was no bonding of the deposited columbium. No further use of the salt filler was planned.

Because of the potential for outgassing of the salt, a slow heating rate was used. Heating was begun at 10:00 a.m. and the targeted CVD temperature was reached at 11:40 a.m. at that time the temperature of the graphite mandrel was reported at 980°C (1796°F) and the panels 920°C (1688°F). The chlorine gas reaction and hydrogen flow was begun. The low viscosity $CbCl_5$ flowed over the carousel and obscured the view. The next temperature reading was at 12:00 noon with the graphite at 1010°C (1850°F) and the panels 970°C (1778°F). This was the highest reading reported for the entire run.

The columbium chips were depleted at 1:18 p.m. for a run time of approximately 90 minutes. The chlorine and hydrogen gas flow was stopped and the argon flow increased for the cooldown.

Depositing columbium at these low temperatures may not be practical. The deposit rate and bond quality may not prove adequate even under proper temperature control.

8.3 CVD RUN NO. 2

Iron and molybdenum powder, some with cavity formers were used in this experiment. The equipment purging was the same as for the first carousel run. Additional thickness, to .38 mm (0.015 inch) thickness of deposited columbium was requested and this required a second cycle to reload the columbium chips in the chlorination vessel. Actually three cycles were performed. The first cycle was interrupted when the chlorination pot cracked 40 minutes into the first cycle. The run times and reported temperatures for each cycle of this second run are as follows:

a) 1125°C (2057°F) to 1150°C (2102°F) - 40 minutes

b) 1140°C (2084°F) - 90 minutes

c) 1130°C (2066°F) to 1140°C (2084°F) - 80 minutes

This 3.5 hour cycle deposited an average columbium thickness of .35 mm (0.014 inches) or .10 mm (0.004 inches) per hour.

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8.3, CVD Run No. 2 (cont.)

8.3.1 Pre-CVD Sintering

The iron and molybdenum filler panels used in this second run were sintered at 1150°C (2102°F) (the planned CVD temperature) for 30 to 45 minutes at 1.0×10^{-6} torr vacuum. This was performed to evaluate the retention of the powdered filler after driving off the acrylic binder and conditioning for surface preparation.

In addition to the eight panels for the carousel, two panels with iron/acrylic powder in the channels were sintered; one in the vertical position and one in the horizontal position. Actual chamber fabrication would require sintering in a vertical orientation. Retention of the sintered iron filler was excellent. Figure 13 shows a section of the panel that had been sintered vertically. The left views at low magnification show the shrinkage of the sintered iron from the channel walls on cool down. These cavities coupled with the inherent sintered iron porosity, greatly accelerated the acid leaching of the iron. The excess iron on the top surface was manually dressed flush with the lands by filing and sanding with Al_2O_3 paper before CVD processing. The lands were cotton swabbed with acetone.

The photomicrographs to the right in Figure 13 show the sintered iron in a 2.39 mm (0.094 inch) channel. There is no evidence of an iron-columbium reaction during the sintering. The Knoop hardness indications, converted to Rockwell, are R_B 80 to 89.

The molybdenum powder has a melting point well above iron, 2620°C (4748°F) and for this reason did not sinter at 1150°C (2102°F) as did the iron. The molybdenum in the channels was slightly powdery after the acrylic cement was vaporized. Only light hand dressing was needed to prepare the surface for the CVD processing.

The eight panels prepared for the second CVD run showed two unusual conditions after sintering. Panel No. 5 which contained the PVC tubing cavity formers showed gas expulsion through the iron and evidence of reaction with the iron. Panels 13 and 14 had four small transverse shrinkage cracks on the large channels. These were repaired with the iron-acrylic slurry applied locally, air dried, dressed flush, and the lands cleaned with acetone.

8.3.2 Iron Filler Results

Panels 14 (iron) and 19 (molybdenum) were sectioned, after columbium deposition, as shown in Figure 14. The top views show a flat, relatively even, deposit of columbium, .35 mm (0.014 inches) thick, over the channels. Somewhat greater shrinkage than that seen for the "as-sintered" condition shown in Figure 13 is apparent. In fact, the lower right photomicrograph shows an agglomerated porous iron structure indicative of temperature exposure in excess of the 1150°C (2102°F) sinter temperature.
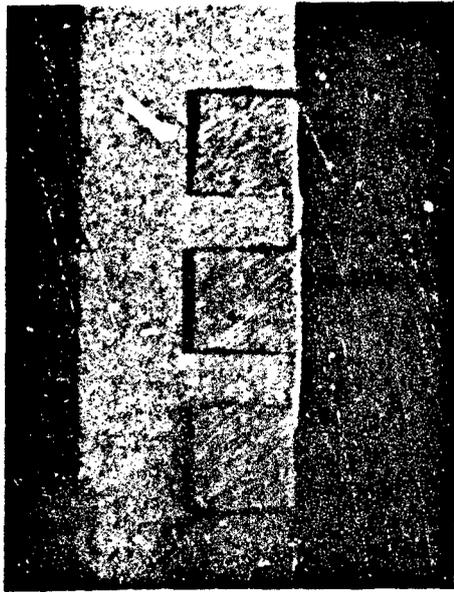
Mag 3X
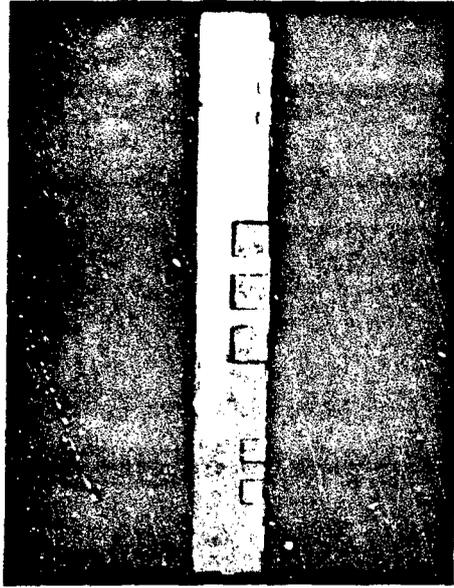
Mag 8X

Mag 100X

Mag 100X

Figure 13. Sintering of Iron/Acrylic Filler Creates Shrinkage Cavity Due to Differential Thermal Expansion with Columbium

36

Mag 8X

Mag 20X

Panel 14 - 094 Channels Iron
Contamination on Land (Arrow)

Mag 80X
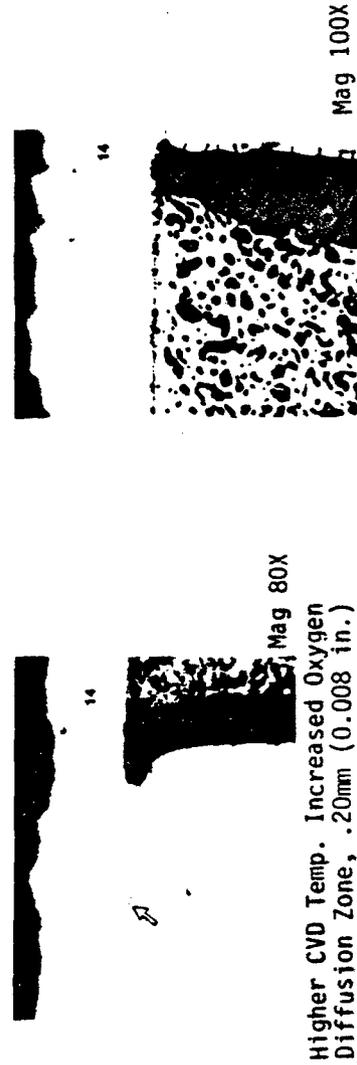
Higher CVD Temp. Increased Oxygen
Diffusion Zone, .20mm (0.008 in.)
Deep

Mag 100X

Porous - Agglomerated Sintered
Iron Indicates > 1150°C Exposure.
Compare with Figure 13.

Figure 14.   Shrink Cavity Formation in the Iron Filled Panel 14 and
Tube Cavity in Center Channel of Molybdenum Filled
Panel 19 After CVD Run 2

37

Also seen in this view is a brittle layer approximately 0.013 mm (0.0005 inches) thick, possibly Cb_3Fe_2 intermetallic compound. No similar reaction was seen after the 1150°C (2102°F) sintering cycle.

Contamination in the bond interface (arrows in the views in Figure 14) degraded the bond quality of the columbium deposit to the C103 substrate. Great care was taken to finish the land preparation in the direction of the lands and cotton swab the area with acetone. Still, the cause of the contamination could be due to smearing of the iron across the lands when dressing down the surface. Later in the program, another potential cause of iron contamination was hypothesized. The free energy of formation may favor the formation of $FeCl_2$ from $CbCl_5$ vapor in contact with the iron, and subsequent reduction of $FeCl_2$ may result in a deposit of iron on the lands. This is discussed in some detail below.

Also shown is the oxygen diffusion zone approximately .20 mm (0.008 inches) deep. This reaction zone has a larger gradient with the higher CVD temperature compared to the first carousel run with copper and salt fillers. In the latter case, the high concentration of oxygen in the surface resulted in a much higher hardness value.

The panels, Nos. 16 and 17, with the slip cast Al_2O_3 coating on the channel walls did not appear to have any metallurgical advantage. Panel No. 16 was used for leaching experiments through the small, 1.57 mm (0.062 inch) diameter back wall holes. Flakes of the Al_2O_3 interfered with acid flow by clogging these access holes.

PVC tubing, with its decomposition product HCl, reacted more than expected with the iron filler. No reaction was experienced with molybdenum, however The innate cavity formation by shrinkage of the iron filler precludes any need for auxiliary methods to create flow passages for the iron.

9.3.3 Molybdenum Filler Results

The molybdenum powder produced good CVD results in that no deleterious reactions of molybdenum with the substrate were observed. Of course, an oxygen reaction zone is present as in all the panels due to oxygen contamination in the system.

The top center photomacrograph of Figure 14 shows a cross section of Panel 19 (Mo) at the three 2.39 mm (0.094 inch) channels. The center channel hole was created through vaporization of the 1.52 mm (0.060 inch) diameter PVC tube. The depression of the deposited columbium on one channel is due to surface preparation and slightly powdery nature of the molybdenum after sintering.

B.3, CVD Run No. 2 (cont.)

The upper views in Figure 15 show unetched and etched sections of an 1.52 mm (0.062 inch) channel from panel 19. The bond appears to be good including examination at higher magnification shown in the lower right view. The upper left etched view again defines the deposit step interruptions in this CVD run and the oxygen zone. This reaction zone is less, approximately .13 mm (0.005 inch) deep as compared to the channels containing iron of .20 mm (0.008 inches). This is probably due to the better oxygen gettering ability of the molybdenum powder.

The lower left view is a section of the "as-deposited" columbium, on the land between 2.39 mm (0.094 inch) channels filled with the Mo/Fe powder, Panel 2. The bond does not appear to be as good as those with the pure molybdenum filler. Some shrink cavity formation was attained, although much less than with pure iron which was anticipated. The mixture does not appear to offer any advantages over pure iron.

B.3.4 Hardness Surveys

Knoop hardness surveys were made on a number of specimens representing panels from this second carousel run. The oxygen diffusion zone appear as a surface reaction on all the exposed areas of the panels as well as the channel surfaces. The reaction zone is of greater diffused depth compared to CVD run 1 at the lower temperature and shorter time. These specimens are of lower surface concentration based on hardnesses of R_B 92 to Rc 34 compared to Rc 51 shown in Figure 12 for Panel 3 of the first run. (All Rockwell hardnesses are converted from Knoop hardness.)

Figure 16 displays Knoop hardness surveys (indicated hardness values converted to Rockwell Hardness numbers) for Panels 14 (Fe), 2 (Mo/Fe), and 19 (Mo). The C103 columbium alloy substrate is R_B 80-85, the columbium deposit R_B 36-38. The surface reaction zone varies from R_B 85 to Rc 34. The hardness indentation in the top center view is at the interface at the start of the second cycle. The higher hardness, R_B 68 versus R_B 35 in the columbium deposit matrix, is probably due to surface contamination on start-up.

The harder surface zones are thought to be oxygen pick-up from air contamination in the reaction chamber, particularly during the heat up cycle in argon. The argon may contain some oxygen and the seals do not appear to be effective with the chamber operating at a reported vacuum of 101.6 mm (4 inches) of mercury.

B.4 CVD RUN NO. 3

This, the final run, was planned as a verification of the effectiveness of iron as a filler and an evaluation of additional cavity formers for molybdenum. Unfortunately, all of the iron containing specimens melted. In some cases, resolidified iron was still present. The run, made at a
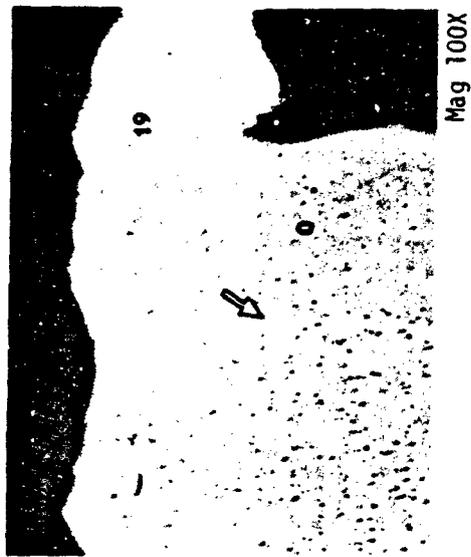
Mag 100X
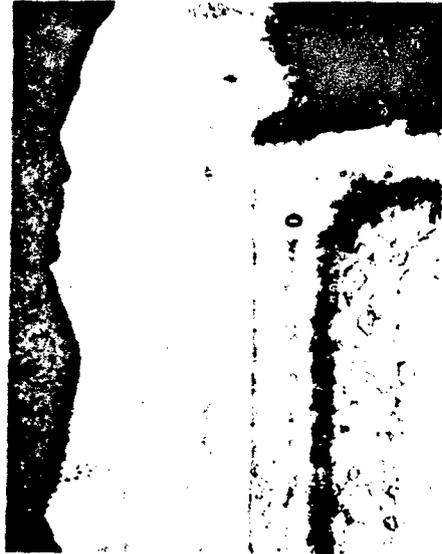
Mag 500X

Mag 100X

Mag 50X

Panel 19 - Bond Line. Etchant H_2SO_4, HF, H_2O_x
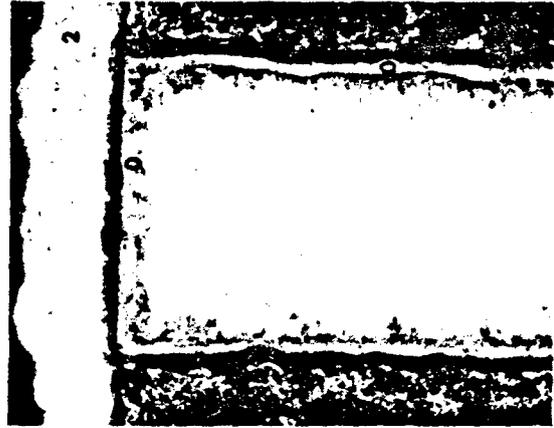
Panel 2 - Mo/Fe Filler Minor Shrinkage

Figure 15. Photomicrographs of CVD Run 2 Mo/Acrylic (19), Mo/Fe/Acrylic (2), and Fe/Acrylic Over Plastic Tubing (17)

40
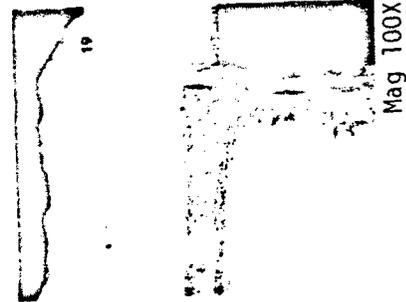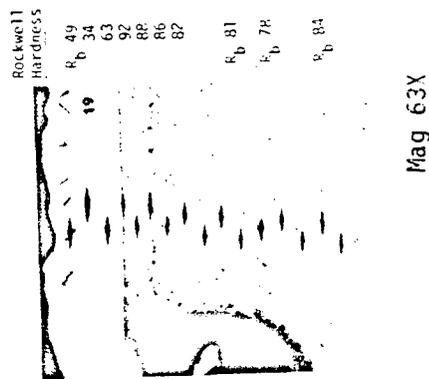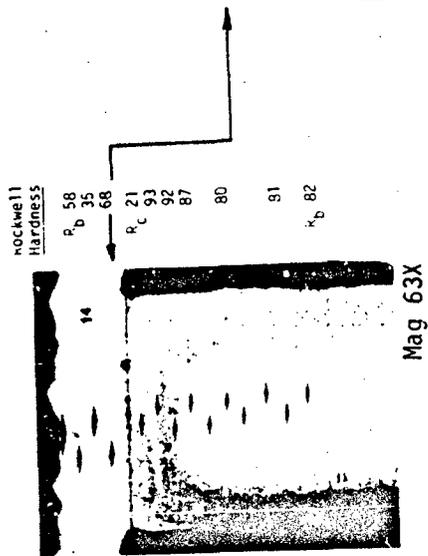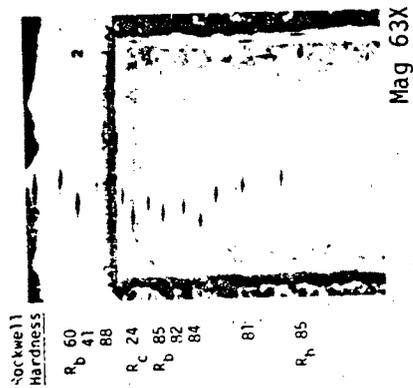
Figure 16. Hardness Survey (Knoop Converted to Rockwell) Across Oxygen Diffusion Zone of Three Panel Sections from CVD Run 2. (Note $R_b 100 \times R_c 20$)

reported temperature of 1150°C (2102°F), lasted for 105 minutes before depletion of columbium in the chlorination chamber. After cool down, the melting was noted and the run discontinued. The condition of six of the eight panels is shown in Figure 17. Only the molybdenum containing Panels Nos. 4 and 22, remained intact.

Panels (23 and 24) containing iron are shown in Figure 18. The top right photomicrograph shows the resolidified iron etched with Nital. The top center is a 1.57 mm (0.062 inch) channel etched for the columbium structure. The "wave shape" of the deposits is another indication of overheating.

The bond interface of the unetched specimens appears better than those of the second run of iron filled panels. This may be due to the greater care exerted in cleaning of the land surfaces after sintering. The lower left view shows the CVD columbium deposited into an .81 mm (0.032 inch) channel after the iron had melted.

The molybdenum filled panels, Nos. 4 and 22, represented two additional attempts to create cavities within the molded molybdenum powder. Although the cottom cording left reasonably large cavities, neither they nor the smaller molybdenum tubes provided any significant improvement in removal of the molybdenum. The overall condition is similar to that found for the molybdenum containing panels of the second carousel run.

Because of the melting of copper occurring on the first run and iron on the third run, differential thermal analysis (DTA) was made on the starting powders. The DTA for copper verified that pure copper was used, melting point 1083°C (1981°F). The DTA for the iron is shown in Figure 19 with the delta iron inflection at 1392°C (2538°F) and the expected melting point for pure iron (1538°C (2800°F)).

Potential causes for lowering the melting point of the iron were evaluated. One is the formation and melting of the columbium-iron eutectic at 1372°C (2502°F), which presupposes a 200°C (392°F) + temperature excursion. Another is melting of the iron-carbon eutectic at 1152°C (2106°F) (4.3%C). However, the acrylic treated sintered iron in the "as-sintered" panels was analyzed for carbon content. The analysis showed 0.09 and 0.12%C present. Another sample of this sintered iron was heated to 1350°C (2462°F) in argon and there was no evidence of melting.

In order to assess potential problems which could occur in vapor deposition process with the use of iron as the filler material in the channels, some thermodynamic calculations were performed using JANNAF THERMOCHEMICAL DATA. Of concern is the reaction of columbium pentachloride with the iron to form a volatile iron chloride which could result in the vapor deposition of iron as well as the columbium metal.

Panels 4 & 22 Contained
Mo/Acrylic Over Cavity
Formers
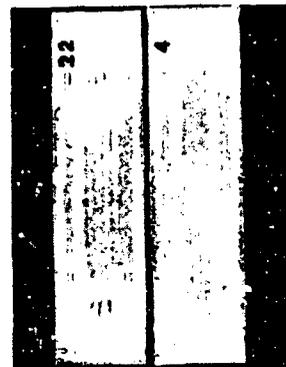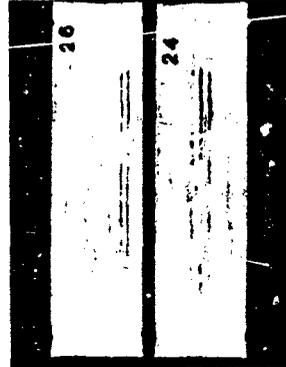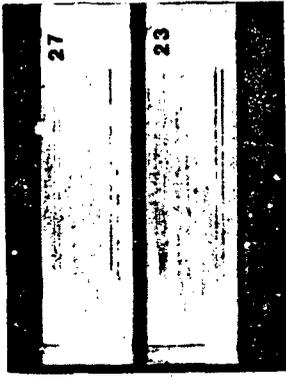
Mag 2.5X

Panel 22 With Cotton Cording
and 4 With Mo. Tubing Cavity
Formers
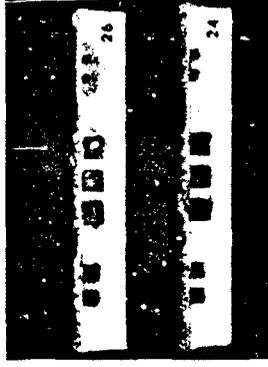
Mag 2.5X

Figure 17.   CVD Run 3 - All Iron Filled Panels Melted
(Nos. 23, 24, 26, and 27 Shown). Panels No. 4
and 22 Contained Molybdenum.

43
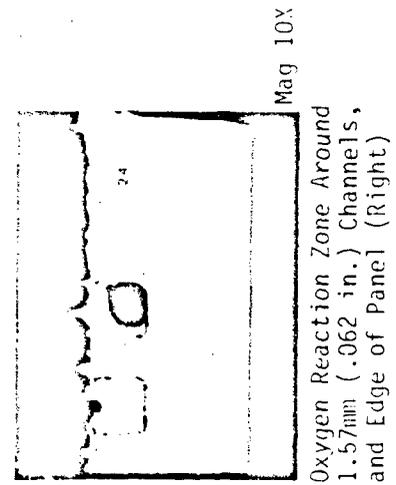
Mag 10X

Oxygen Reaction Zone Around
1.57mm (.062 in.) Channels,
and Edge of Panel (Right)
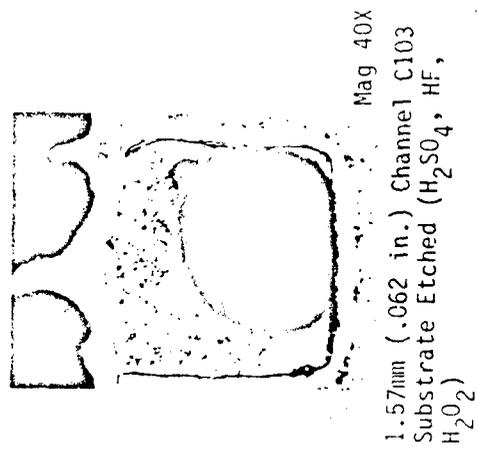
Mag 40X

1.57mm (.062 in.) Channel C103
Substrate Etched (H_2SO_4, HF,
H_2O_2)
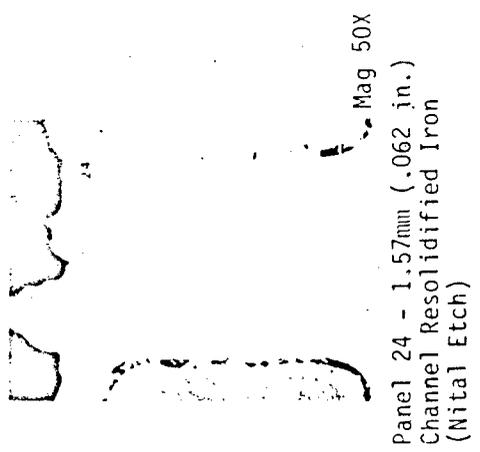
Mag 50X

Panel 24 - 1.57mm (.062 in.)
Channel Resolidified Iron
(Nital Etch)

Mag 50X

.81mm (.032 in.) Channel
Iron Melted Out and Cb
Deposited in Channel
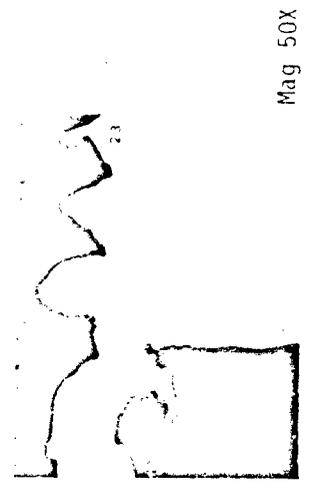
Mag 50X

Panel 23 - 2.39mm (.094 in.)
Channel Unetched Shows
Good Bond

Figure 18. Photomicrographs of Panels 23 and 24 Showing
Effects of Iron Melting During CVD Run 3

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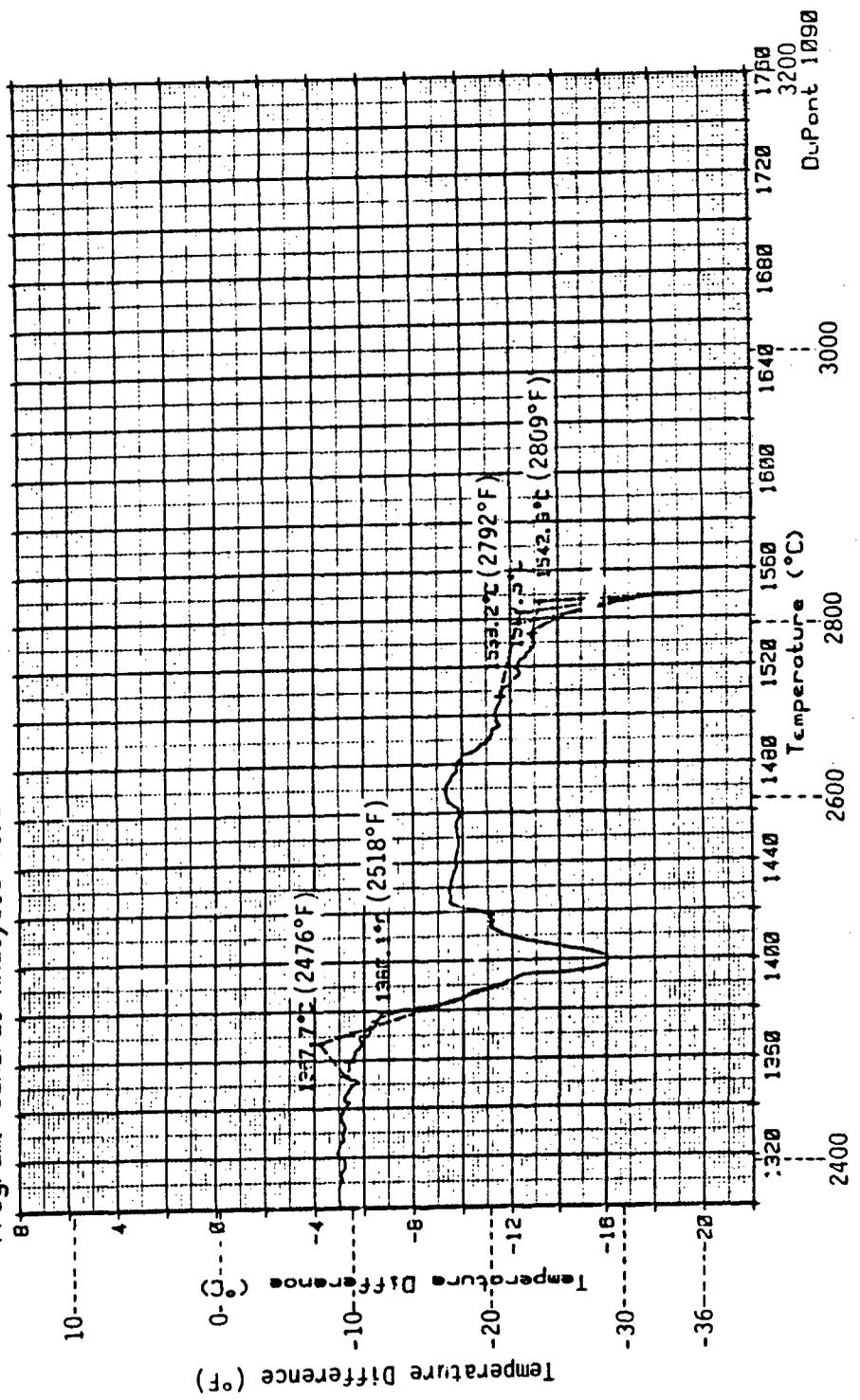
Figure 19. Melting Point Determination for Iron Powder

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The data for the reaction

$$3 \, CbCl_5(g) + 5 \, Fe_{(s)} \rightleftharpoons 5 \, FeCl_3(g) + 3 \, Cb_{(s)}$$

indicate that it will not occur. However, the data for the other reaction

$$2 \, CbCl_5(g) + 5 \, Fe_{(s)} \rightleftharpoons 5 \, FeCl_2(g) + 2 \, Cb_{(s)}$$

over the temperaure range from 1300K (1023°C (1880°F)) to 1600K (1323°C (2420°F)) yield free energy values ranging from -13.496 to -49.897 kcal mole^{-1}, respectively, and the log Kp values range from +2.27 to +6.81,

$$\text{where } Kp = \frac{[FeCl_2(g)]^5}{[CbCl_5(g)]^2} \; ;$$

[FeCl$_2$(g)] is the partial pressure of ferrous chloride in the system, and

[CbCl$_5$(g) is the partial pressure of columbium chloride in the system.

The Kp values indicate that the formation of ferrous chloride is favored in the reaction as written.

Because FeCl$_2$ is readily formed by the reaction of iron with CbCl$_5$ in this temperature range, the extent of the problem depends on whether the presence of hydrogen in the system, with the subsequent formation of HCl, will prevent significant attack of the iron.

The data for this reaction

$$H_2(g) + FeCl_2(g) \rightleftharpoons Fe_{(s)} + 2HCl(g)$$
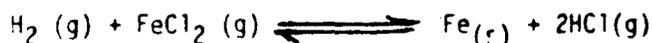
over the temperature range from 1300K (1023°C (1880°F)) to 1600K (1323°C (2420°F)) yield free energy values ranging from -1.788 to -0.317 kcal mole^{-1}, respectively, and the log Kp values range from +0.3005 to +0.04331. This reaction is favored to occur, but a significant concentration of FeCl$_2$ can exist at equilibrium conditions.

The amount of iron which can be transported in the process can be minimized by maintaining the temperature at a value as low as practical during the initial stage of the process and by maintaining an adequate hydrogen concentration in the system at the initiation of the process. There is no metallographic evidence of iron contamination on the molybdenum fiiled panel 19 which was run with the iron filled panels. This iron reaction and possible deposition would be a very localized condition.

8.0, CVD Test Results (cont.)

8.5 FILLER MATERIAL REMOVAL

Successfully coated panels from each of the CVD runs were evaluated for leaching rate. Ten panels, representing the basic salt filler, salt and iron mixture, iron, and molybdenum were tested. Three of these panels were not sectioned, Nos. 13, 16, and 19, but were leached from the backside through the 1.57 mm (0.062 inch) diameter holes at each end of the three 2.39 mm (0.094 inch) square channels (see Figures 5 and 6). The balance of the panels were sectioned 50.8 mm (2 inches) back from one end exposing the filled channels. These channels have a three inch length. Five of the panels were tested using a peristaltic pump to direct the acid into the channels. The balance were tested for dissolution rate by static immersion.

The leaching rate data for these panels is given in Table 5. Selected channels were leached with the stated media and depth of filler removal measured at the indicated times.

The iron fillers dissolved at a relatively fast rate, especially where the acid was directed by pumping through a 0.004 inch I.D. stainless steel tube (Panel 14). Panel 13, leached by immersion through the back-side holes, cleared the 2.39 mm (0.094 inch) square channels in 150 minutes. The aluminum oxide wash, Panel 16, apparently interfered with the acid flow by clogging the small 1.57 mm (0.062 inch) diameter holes.

The molybdenum filled channels all displayed a very low to negligible leach rate. The hot dilute nitric acid would begin the reaction and MoO_3 formation would delay further action. Panel 19 was alternately immersed in ammonium hydroxide to dissolve the oxide then exposed again to nitric acid. Slight improvement in the rate was seen. The molybdenum/iron mixed powder had a good leaching rate with the acid pumping.

The cavities in molybdenum filled channels 4 and 22 were not effective in increasing the rate of dissolution of that filler material. The center channel of Panel 19 was effective but producing passages of the same relative size in the small throat section channels does not appear practical. Another leaching solution, potassium ferricyanide, was tried and also was not satisfactory.

8.6 SEM/EDX EXAMINATION

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) spectroscopy was employed in an attempt to identify the contaminants and reaction products. Figure 20 is the Panel 14 C103 substrate. (C103 columbium alloy contains 10% hafnium (Hf) and 2% titanium (Ti).) The bond line inter-

TABLE 5. LEACHING TESTS ON CVD PROCESSED COLUMBIUM TEST PANELS

Panel No.	Filler Material	Leaching Media	Time, Min.	Leaching Rate, g/cm²/min Channels[1]						
				1	2	3	4	5	6	7
3	50/50 K_3PO_4/Al_2O_3 (Basic Salt)	H_2O 100°C (212°F)	5	-	-	0.98	0.98	0.98	0.38	0.38
			15	-	-	0.69	0.69	0.69	0.29	0.29
			20	-	-	0.69	0.69	0.69	0.38	0.38
			135	-	-	0.17	0.17	0.17	0.03	0.03
						(2 Channels Open; 1 Channel Partially Open)				
6	55% Fe/45% Basic Salt	50/50 HNO_3/H_2O 40.6°C (150°F)	60	-	-	0.19	0.19	0.19	0.13	0.13
13	Fe/Acrylic	50/50 HNO_3/H_2O 40.6°C (150°F) From Back Holes (Note 2)	150	-	-	0.34	0.34	0.34	-	-
						(Channels Open)				
14	Fe/Acrylic	50/50 HNO_3H_2O 40.6°C (150°F) (Note 3)	5	-	-	5.88	-	3.69	-	-
			8	-	-	5.53	-	-	-	-
						(Channel Open)				
			10	-	-	-	-	2.43	0.35	-

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TABLE 5. LEACHING TESTS ON CVD PROCESSED COLUMBIUM TEST PANELS (cont.)

Panel No.	Filler Material	Leaching Media	Time, Min.	Leaching Rate, g/cm²/min Channels(1)						
				1	2	3	4	5	6	7
14 (cont.)			13	-	-	-	-	2.20	-	-
								(Channel Open)		
			23	-	-	-	-	-	0.54	-
			72	-	-	-	-	-	0.35	-
16	Fe/Acrylic Al Oxide Wash	50/50 HNO₃/H₂O 40.6°C (150°F) From Back Holes (Note 2)	240	(Water under pressure would ooze through the fill material. No improvement after 1140 minutes. Al₂O₃ flakes clogged 1.57 mm (.062 in.) diameter back side holes.						
18	Mo/Acrylic	50/50 HNO₃/H₂O 40.6 C°(150°F) From Back Holes (Note 2)	1140	(After 1140 minutes there was still no flow through any of the channels.)						
2	66-2/3 Mo/ 33-1/3 Fe/ Acrylic	50/50 HNO₃/H₂O 40.6°C (150°F) (Note 3)	3	-	-	-	-	-	-	0.38
			5	-	-	-	1.34	2.58	-	-
			15	-	-	2.45	-	-	-	-
			21	-	-	2.18	-	-	-	-
			27	-	-	1.76	-	-	-	-
			41	-	-	-	-	-	-	0.10

TABLE 5. LEACHING TESTS ON CVD PROCESSED COLUMBIUM TEST PANELS (cont.)

Panel No.	Filler Material	Leaching Media	Time, Min.	Leaching Rate, $g/cm^2/min$ Channels(1)						
				1	2	3	4	5	6	7
19	Mo/Acrylic	50/50 HNO$_3$/H$_2$O 40.6°C (150°F) (Note 3)	45	-	-	.006	-	-	-	-
			65	-	-	.008	-	-	-	-
				NOTE: Pumping Discontinued. Cb Deposit removed exposing wide zone for acid immersion.						
		Immersion	40	0.09	0.09	0.15	0.90	0.12	0.09	0.07
			162	0.03	0.03	0.06	0.29	0.04	0.04	0.02
			342	-	-	0.03	-	-	-	0.02
			537	0.009	0.009	0.03	-	0.01	0.02	0.01
4	Mo/Acrylic Over Acrylic Tubing	50/50 HNO$_3$/H$_2$O 40.6°C (150°F) (Note 3)	105	.004	.004	.006	.006	.006	.003	.003
22	Mo/Acrylic Over Cotton Cording	50/50 HNO$_3$/H$_2$O 40.6°C (150°F) (Note 3)	105	.004	.004	.006	.006	.006	.003	.003

NOTE 1. Channels 1 & 2 are .81 mm (.032 in.); 3, 4, & 5 are 2.39 mm .094 in.); 6 & 7 are 1.57 mm (.062 in.)

NOTE 2. Leaching of channels 3, 4, 5 from back side 1.57 mm (.062 in.) diameter holes only.

NOTE 3. Acid pumped into channels with peristaltic pump through .10 mm (0.004 in.) I.D. tubing.

Figure 20. EDX Spectra of Panel 14 C103 Substrate

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face spectra of Panel 14 is given in Figure 21. There was an indication of oxygen at the interface. Iron was not identified on this mount possibly because micrograph preparation removed any iron contaminant on that surface. The carbon peak is from the carbon ccating applied to the mount to make the bakelite mounting material electrically conductive.

Figure 22 is a point spectra on the .013 mm (0.0005 inch) thick layer adhering to the side wall of the Panel 14 large channel (refer to lower right view of Figure 14). This spectra shows a large iron peak indicative of a columbium-iron intermetallic compound. Lack of Cb-Fe intermetallic standards prevented verification of intermetallic formation.

In addition to the metallographic mounts, sections of the Panel 14 were examined on the C103 land surface after mechanical removal of the CVD columbium deposit. Significant evidence of iron present on the land as well as oxygen is shown in Figure 23. The same evidence of iron and oxygen was found on the exposed land surface of Panel 27 from the third carousel run.

Oxygen could not be detected at the near surface reaction zone seen in all the photomicrographs. The SEM/EDX is not sufficiently sensitive to pick up low oxygen contents. However, the presence of oxygen was shown in several spectra of land surfaces.

Figure 21. EDX Spectra of Panel 14 Bond Line Interface

```
06-MAR-84 16:11:28 EDAX READY
RATE:      4452CPS TIME        50LSEC
00-20KEV:10EV/CH PRST          50LSEC
A 14M SDWL 20KV B:
FS=      3065    MEM: A    FS=      200
|00        |02        |04        |06        |08
```

Fe

Nb

Si

Fe
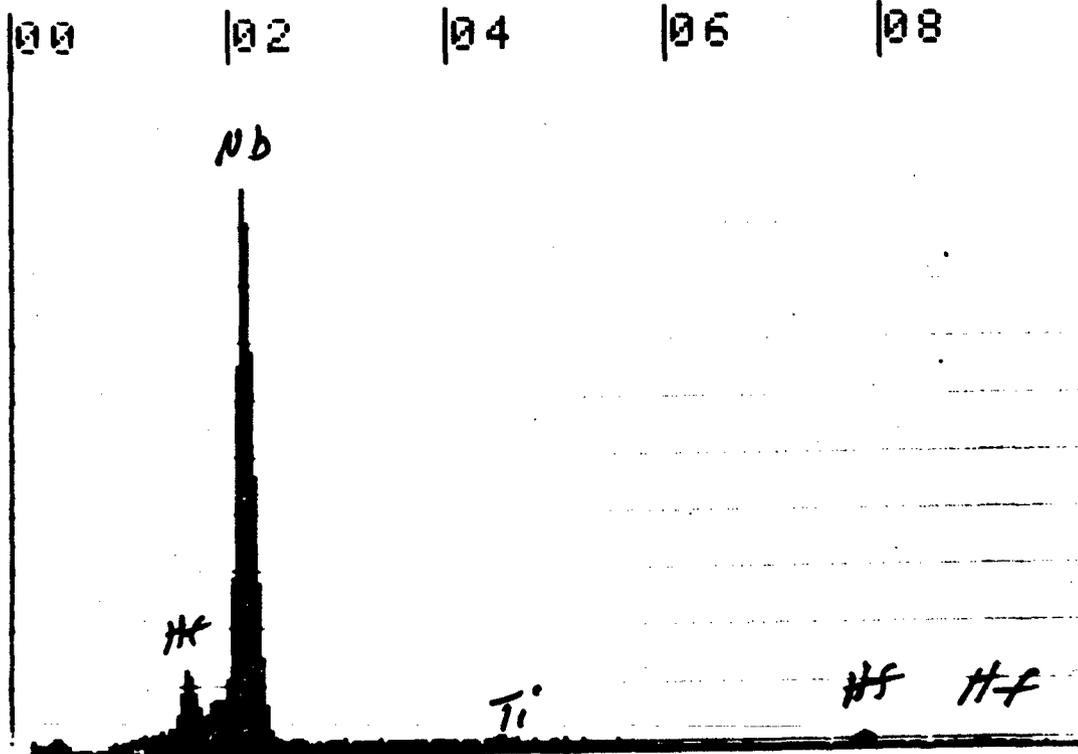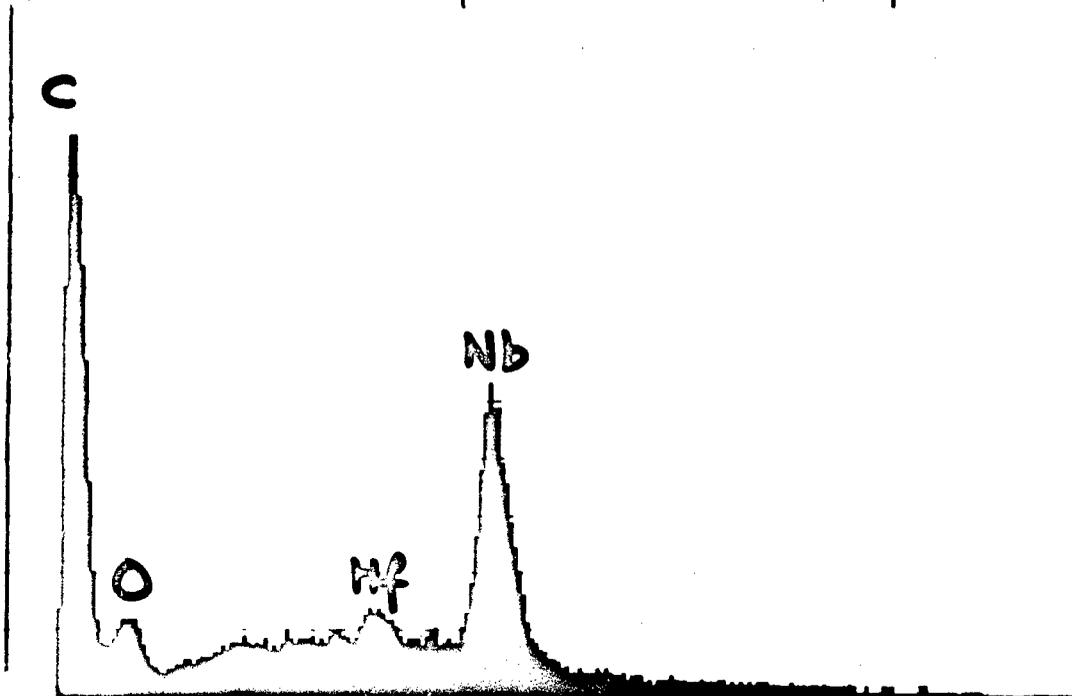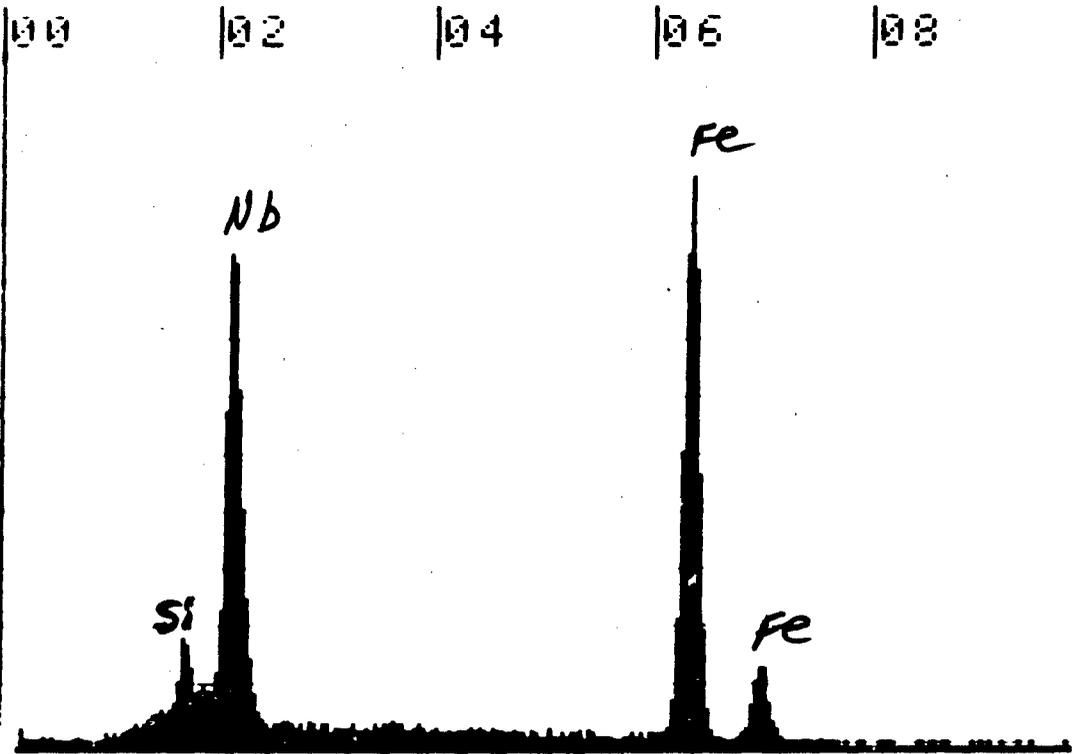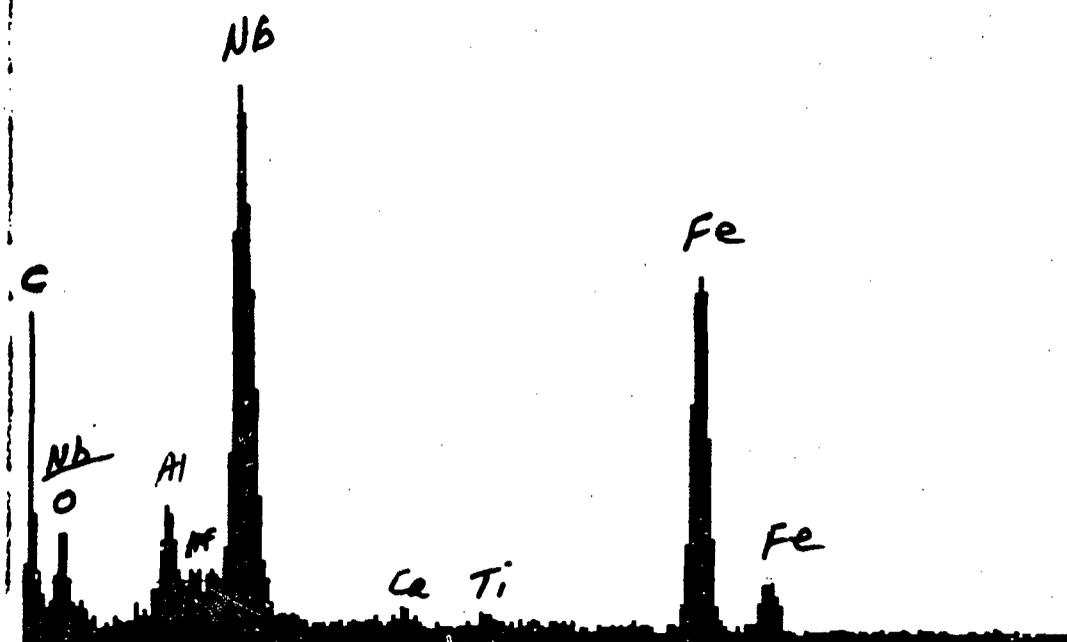
```
CURSOR (KEV)=05.120                EDAX
```

```
FILENAME(MAX 6 CHARS):14MSW2
```

Figure 22. EDX Spectra of Panel 14 Channel Wall

Figure 23.   EDX Spectra Panel 14 Land Surface

SECTION 9.0 DISCUSSION

The temperature restriction on the use of copper filler material eliminates what was hoped to be an easily applied and, post-CVD removable filler material. Low deposition rates and anticipated marginal bond quality at the lower temperature, even with required temperature controls, does not seem to justify continued development effort for copper.

The K_3PO_4 salt was attractive because of its high melting point and easy dissolution in water. The hygroscopic effect could be minimized by direct transfer of the hot baked salt filled specimen (on chamber) directly to the CVD reaction chamber. However, application and preparation of the salt mixtures due to the shrinkage, handling, and transporting difficulties coupled with the heating lag due to low inductance also require development work. None of the salt filled panels bonded.

Molybdenum is the filler material most compatible with the substrate and the CVD environment. However, it appears impractical because of its leaching characteristics.

Iron powder molded in place and with its sintered shrinkage cavities is the most promising filler candidate. The reactive nature of iron permits leaching but also presents problems of compatibility witn the system. However, the reaction of the iron filler reported herein is largely due to excessive temperature during the CVD processing. Evidence of temperatures in excess of the planned 1150°C (2102°F) in the second run was verified by even greater temperature excursions which melted the iron specimens in the third run.

The melting point of the filler may have been suppressed somewhat by some gaseous or solid state reaction during the CVD process, however, it is believed that the required conditions for such a reaction are significantly higher than 1150 C (2101'F).

The contamination of the bond interface with iron needs to be addressed and can be overcome. A technique to seal the iron from the CVD atmosphere can be accomplished. One method would be to dress the sintered iron filled channels to just below the adjacent land surface. A preliminary thin deposit of columbium would be applied over the entire surface. Subsequently, the lands would be axially milled to expose a fresh C103 land surface. The unit, with the iron filler sealed with columbium would then be CVD processed and a sound bond obtained.

Modification of the CVD apparatus is needed to obtain a true temperature control. The oxygen contamination is believed to be occurring during the heat-up cycle in the low pressure argon atmosphere. It is possible to have a slightly positive argon pressure during the heat up phase and with better seals the oxygen contamination can be eliminated.

SECTION 10.0 CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. Iron powder, molded into the channels with acrylic cement, best fulfills the overall requirements of application, handling, and post-CVD leaching for a filler for columbium CVD close-out.

2. CVD processing of chambers with fillers requires improved process controls. The normally employed optical pyrometry does not adequately control temperature.

3. Molybdenum is the most compatible filler but cannot be adequately removed.

4. Methods of creating flow cavities within the molybdenum filled channels are difficult to apply to chambers. Cavities produced did not resolve leaching problems.

5. Machining of lands after filling is required to prevent contamination at CVD deposit bond interface.

6. Temperature limitation with copper fillers reduces deposit rate and bond quality.

7. Water soluble salts cannot be adequately controlled to prevent moisture and gas evolution during CVD processing.

RECOMMENDATIONS

1. Modify the CVD apparatus to permit direct contact (thermocouple) temperature measurement. Improve seals and system atmosphere to eliminate oxygen contamination.

2. Use iron/acrylic for channel filler and seal the iron with a thin columbium deposit. Machine mill the coating from the lands to expose fresh substrate surface. CVD complete the close-out over the sealed iron filler with CVD columbium.

3. Proof test channels to evaluate bond strength of coating.

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